

Dipartimento di Fisica Facoltà di Scienze Matematiche, Fisiche, Fisiche e Naturali

UNIVERSITÀ DEGLI STUDI DI TRENTO

Negative Thermal Expansion in Zincblende Structure: an EXAFS study of CdTe

A thesis submitted for the degree of Doctor of philosophy in Physics

By

Naglaa Fathy Abd El All

Supervisors

Prof. Giuseppe Dalba Prof. Paolo. Fornasini

Ph. D. Thesis in Physics, XXIII cycle 2010

To my husband and my sons

Acknowledgement

I am indebted particularly to my supervisor Prof. Giuseppe Dalba for inviting me to join his research group at the University of Trento. I am also grateful to my supervisor, Prof. Paolo Fornasini, who exercised, with his great experience and deep knowledge, and extraordinary patience throughout the full working of the data analysis and discussions. Thanks so much for their friendship, their scientific insight, their wisdom and knowledge of humanity and provided an excellent atmosphere for our academic work.

Special thanks to Prof. Rolly Grisenti whose perceptive comments and advices help for learning new programs during the data analysis. I would also like to extend my thanks to Dr. Francesco Rocca for his assistance in the measurements and his cooperation throughout the research.

My special thanks to the group of the X-Ray Synchrotron Radiation Laboratory at Trento University for providing all the facilities needed and for their great deal of cooperation.

I would like to thank so much my friends "A. Saidane, F. aboareef and S. arfaoui" about their supporting me and living in a family atmosphere in Trento.

There are neither words nor deeds to thank my mother and my father also my brothers and all my family for helping and supporting me during three years. I am indebted particularly to my brother's wife "Karema" for caring my young child during three years with all the lovely mother feelings.

I dedicate this work to my husband "Mohamed" and my sons "Ahmed and Belal" in the hope that i express my deep feelings of love and gratitude to them.

Contents

Co	Contents									
In	Introduction									
1	Negative Thermal Expansion (NTE)									
	1.1	Introd	uction	5						
	1.2	Therm	nodynamic relations	10						
	1.3	1.3 Quasi-Harmonic Approximation		13						
	1.4	1.4 Vibrational mechanisms in thermal expansion		16						
		1.4.1	Central force mechanisms	17						
		1.4.2	Non-Central force mechanism	21						
	1.5	EXAF	S studies of the NTE	22						
2	EX.	AFS a	nd Thermal properties	25						
	2.1	S technique	25							
		2.1.1	Introduction	26						
		2.1.2	XAFS: X-ray Absorption Fine Structure	28						
		2.1.3	The EXAFS mechanism	31						
2.2 EXAFS equation		S equation	34							
		2.2.1	Many body effects	40						
		2.2.2	Thermal disorder effects	42						
		2.2.3	Cumulant expansion of EXAFS	44						
2.3 EXAFS and local dynamics			S and local dynamics	47						
		2.3.1	Cumulants and lattice dynamics	48						

	2.4	EXAFS versus Bragg diffraction							
		2.4.1	Interatomic distances	51					
		2.4.2	Thermal factors	52					
		2.4.3	Anisotropy of vibrations	55					
	2.5	Phenomenological models for EXAFS MSRDs							
		2.5.1	Correlated-Einstein model \ldots	58					
		2.5.2	Correlated-Debye model	59					
	2.6	EXAF	S and Anharmonic potential	61					
		2.6.1	Classical approximation	62					
		2.6.2	Quantum treatments	63					
		2.6.3	Thermal expansion	64					
3	NT	NTE in Tetrahedrally bonded crystals							
	3.1	Introd	uction	67					
	3.2	2 Elastic properties of Zincblende structure							
		3.2.1	Valence-Force Field model (VFF)	74					
	3.3	NTE in zincblende structure							
	3.4	EXAF	S studies of NTE zincblende crystals	80					
4	EXAFS OF CdTe 83								
	4.1	EXAF	S Experiment and data reduction	83					
		4.1.1	Sample preparation	83					
		4.1.2	EXAFS Measurements	84					
		4.1.3	EXAFS data reduction procedure	86					
		4.1.4	Extraction of EXAFS signal	86					
	4.2	Fourie	r Transform	89					
		4.2.1	The direct Fourier transform $(k \text{ to } r)$	89					
		4.2.2	Back Fourier transform (r to k) $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	90					
	4.3	Quant	ative Analysis procedures	92					
		4.3.1	ratio method	94					
		4.3.2	FEFF6-FEFFIT method	98					
	4.4	First S	Shell EXAFS Cumulants	103					

		4.4.1	First Shell: Thermal expansion	105	
		4.4.2	First Shell: Mean Square Relative Displacements	107	
		4.4.3	First Shell: MSRDs and MSDs	110	
		4.4.4	First Shell: Asymmetry of the distance distribution	113	
	4.5	Outer	Shell Analysis	116	
		4.5.1	FEFF6-FEFFIT method	116	
		4.5.2	Ratio method	117	
5	Dis	scussion			
	5.1	Comparison EXAFS-XRD: Thermal Expansion			
		5.1.1	EXAFS first cumulant and crystallographic expansion	124	
		5.1.2	EXAFS third cumulant	126	
		5.1.3	Thermal expansion from potential anharmonicity	129	
		5.1.4	Thermal expansion of outer shells	130	
	5.2	2 Comparison EXAFS - XRD: Thermal Factors			
		5.2.1	Anisotropy: MSRDs - MSDs	133	
	5.3 Corr		ation effects: EXAFS versus XRD	136	
		5.3.1	Connection: MSRDs - NTE properties	139	
	5.4 Comparison: EXAFS - VFF model		arison: EXAFS - VFF model	143	
		5.4.1	Bond Stretching	143	
		5.4.2	Bond Bending	145	
		5.4.3	General comments	147	
Conclusions					
Bibliography					

Introduction

Thermal expansion is a critical parameter and a basic physical property in many scientific and technological applications [1]. Although most materials exhibit positive thermal expansion, some materials have negative thermal expansion in some temperature interval. Negative and low thermal expansion materials have important potential uses in many applications; e.g. electronic devices, dental applications, substrates for high-precision optical devices.

NTE phenomenon is generally considered to be unusual and limited to certain types of structures. The most familiar example of negative thermal expansion is given by water. Liquid water exhibits an increase in density when heated between 273K and 277K whilst the hexagonal form of ice has a NTE coefficient around 45K [2]. It is known since long time that many tetrahedrally bonded semiconductors with the diamondzincblende structure exhibit NTE in restricted low-temperature intervals [3], the NTE strength and interval increasing with the bond ionicity; CuCl exhibits the strongest NTE ($\alpha_{min} \sim -8 \times 10^{-6} K^{-1}$). NTE in zincblende crystals has been attributed to the presence of low-frequency transverse vibrational modes with negative Grüneisen parameter, whose effect is dominant in a limited temperature interval [4].

The interest towards NTE has been renewed in the last decade [1,5,6] by the discovery of some materials with framework structures exhibiting strong NTE over large temperature intervals, such as ZrW_2O_8 , which contracts from 0.3 to 1500K [7]. NTE in framework structures has been attributed to the influence of strong vibrations perpendicular to some interatomic bonds and can often be connected to the low-frequency rigid unit modes (RUM), that cause a rotations of the basic polyhedral units [8]. The attention of the applied research on NTE has focussed on the search for new composite materials with specifically tailored thermal expansion properties to meet specific thermal expansion requirements [1,5].

The recent discoveries have also renewed the interest for a deeper basic understanding of the mechanisms at the origin of NTE. According to a widely accepted phenomenological model, the observed macroscopic expansion is the net result of a competition between a positive bond stretching contribution due to the anharmonicity of the effective pair potential and a negative contribution due to tension effects [6]. When tension effects prevail over bond stretching, solid contract upon the heating.

EXAFS spectroscopy is particularly suited to study the thermal properties of selected atomic species, owing to its selectivity of atomic species, insensitivity to long range order and sensitivity to correlation of atomic motion [9–11]. Recently, new perspectives for getting a deeper insight on the local origin of NTE have been obtained from the progresses in EXAFS analysis and interpretation ([12] and references therein), that led to the possibility of accurately measuring (a) the thermal expansion of the nearest neighbors bond distance and (b) the perpendicular mean square relative displacement (MSRD) and the anisotropy of relative vibrations.

The EXAFS studies recently performed on several crystals with different structures (diamond-zincblende, cuprite and delafossite) suggested that within each family of isostructural compounds a correlation can be established between NTE properties and several quantities measured by EXAFS: bond thermal expansion, parallel and perpendicular mean square relative displacements, anisotropy of relative displacements and correlation of vibrational motion. The analysis of the common features shared by these different crystal structures, and their relation to NTE properties suggested an interpretation within the framework of the phenomenological model based on the competition between stretching and tension effects [13]. For all studied crystals, the bond thermal expansion measured by EXAFS was larger than the lattice expansion measured by diffraction and also different from the thermal expansion solely determined by the asymmetry of the effective pair potential [14]. Recently, Path Integral Monte Carlo (PIMC) calculations for copper have confirmed that the bond thermal expansion depends not only on the asymmetry but also on a rigid shift of the distance distribution.

The origin of NTE is quite intuitive for crystal where linear links (A-B-A) are present and anisotropic thermal factors are found by diffraction for the central atom B; vibrations perpendicular to the A-B-A direction are more intense than parallel vibrations. In cuprite and delafossite structures, EXAFS measurement have revealed that the anisotropy of the relative displacement of atom B is much stronger than the anisotropy of the absolute displacements measured by diffraction. The perpendicular to parallel MSRDs anisotropy is larger for crystals with stronger NTE. In the diamondzincblende crystals the situation is more complex in view of the non-linear character of the (A-B-A) links and of the coordination of each atom to four nearest-neighbors atoms. Also the atomic thermal ellipsoids measured by Bragg diffraction in zincblende crystals are isotropic for symmetry reasons. The recent EXAFS results on Ge and CuCl have shown that a correlation can be established between NTE properties and several quantities measured by EXAFS.

To gain a deeper insight on the local origin of NTE in zincblende crystals and confirm the suggested correlation, EXAFS measurements have been performed on CdTe, which has NTE properties intermediate between Ge and CuCl. In this work an accurate evaluation of the bond thermal expansion, parallel and perpendicular MSRDs and distribution asymmetry of the first shell of CdTe has been made, obtaining a good agreement between two different procedures of the data analysis (i) ratio method (ii) FEFF6-FEFFIT method. The values of the relevant parameters of CdTe were found intermediate between the corresponding values previously found for Ge and CuCl. A critical comparison of EXAFS and Bragg diffraction results; thermal expansion, thermal factors and correlation of atomic vibration, for the iso-structural crystals Ge, CdTe and CuCl has been performed. The correlation between several quantities measured by EXAFS and NTE properties is confirmed.

The work consists of five chapters, organized as follows:

- Chapter 1 contain a general introduction to the phenomenon of negative thermal expansion (NTE) in crystals both from the thermodynamics and the microscopic points of view.
- Chapter 2 is devoted to a review of the EXAFS technique and of its capabilities to study the local dynamics of materials. The differences between EXAFS and XRD concerning interatomic distances and thermal factors are explained as well as the relation between EXAFS cumulants and force constants of one-dimensional effective pair potential.
- Chapter 3 is dedicated to negative thermal expansion in tetrahedrally bonded crystals. The attention is focused on the elastic properties of zincblende structure and on their dependence on bond ionicity. The Valence force field model is introduced.
- Chapter 4 presents our EXAFS study of CdTe: measurements procedures, data analysis by the ratio method for the 1st shell and by non-linear fitting procedure for the first three shells. Bond thermal expansion, MSRDs and asymmetry of distance distributions are presented and compared with both theoretical models and Bragg diffraction results
- Chapter 5 is dedicated to a comprehensive discussion and a critical comparison of the CdTe results with the previously studied crystals, Ge and CuCl. Asystematic study is done of the correlation of the different quantities measured by EXAFS and Bragg diffraction with the NTE properties of the three crystals. At last, a comparison between the effective force constants measured by EXAFS and the force constants of the VFF model is performed as a function of the ionicity.

Chapter 1

Negative Thermal Expansion (NTE)

1.1 Introduction

Thermal expansion is a critical parameter and a relevant property for a wide variety of technological applications as micro mechanics, electronic devices, biomedical materials and others [15]. Most of the materials expand when heated and exhibit positive thermal expansion (PTE), i.e. the volume is increased (density decreases) but in fact there are some materials that exhibit Negative Thermal Expansion (NTE) and contract in some particular temperature range. In spite of decades of experimental and theoretical studies [3,15] of the NTE phenomenon, only recently has particular attention been focused on this phenomenon and the materials which exhibit NTE over large temperature ranges [1,4]. The interest for these materials is related to the possibility of obtaining composite materials with a specific coefficient of thermal expansion, positive or negative or zero in some specific temperature range.

The NTE phenomenon is found more often in solids. In all solid materials the atomic vibrations contribute to the heat capacity and thermal expansion. The contraction of solids on heating seems anomalous and against the common idea that atoms need more room as the vibrational amplitude increases. The popular explanation for thermal expansion is based on the model of anharmonic pair potentials between atoms [16] as shown in Fig. (1.1). When the atoms vibrate along a line connecting the pair, the asymmetry in the potential causes an increase in the mean distance between the atoms as the temperature increases. This gives the interpretation of the most important mechanism for positive thermal expansion, and correctly indicates that atomic vibrations give rise to thermal expansion only because of anharmonicity.

One can see that this model strictly applies only to isolated diatomic molecules; the asymmetry of the interaction potential energy induces positive thermal expansion in two-atomic molecules. But in many atomic system like crystals, where potential is defined in a many-dimensional configuration space, the situation is more complex and thermal expansion can also be negative.

The weakness of this model that considers only the component of relative vibrational motion directed along the line joining the atoms, so it cannot account for negative thermal expansion. There are also components of relative motion perpendicular to this line that tend to decrease the distance between the mean positions of the two atoms, and so to contract the solid.

In addition, non-vibrational (electronic, nuclear etc) contributions to the thermodynamic properties can also cause spectacular effects, particularly at low temperatures where the vibrational contributions are small.

Negative thermal expansion is usually found in materials with relatively open structure, where coordination numbers N are small. These open structures offer sufficient free room for perpendicular vibrations and then for the tension effects, which lead to NTE when these vibrations predominate, as will be discussed below (see sec. 1.4). Therefore, NTE is not found in close packed (N = 12) and body centered cubic (N = 8) structures and it is very weak and rarely observed among the alkali halides with rock salt structure (N = 6) [6,17] while a considerable NTE can occur in tetrahedrally coordinate structures (N = 4) and in crystals where some atoms show low coordination (e.g. N=2), like in framework structures.



Figure 1.1. Interatomic potential: when the temperature increases, the asymmetry due to the anharmonicity causes an increase in the mean value of the bond length (crosses) and give rise to positive thermal expansion.

It is known since long time that NTE affects several simple crystals with diamond and zincblende structures like Si, Ge or CuCl in restricted low temperature intervals [3]. According to a commonly accepted phenomenological model, the macroscopic expansion is the result of a competition between a positive contribution due to bond stretching effect and negative contribution due to tension effects [6]; when the tension effects prevail over the bond stretching effect, the solid contracts. In zincblende structure the tension effect prevails only at low temperatures and is progressively overcome by the stretching effect when temperature increased [18], the strength and temperature interval of NTE depending on their ionicity (see details in Chapter 3).

In the last decade, the discovery of some framework structures that undergo NTE over extended temperature intervals as ZrW_2O_8 [7], and $Zn(CN)_2$ [1] has renewed the interest for NTE from both the fundamental and the technological points of view [1, 5, 6]. Materials exhibiting strong NTE are generally characterized by framework structures [19] made up by networks of corner-sharing polyhedral units [13, 20], the best example of large isotropic NTE material was found in the cubic zirconium

tungstate ZrW_2O_8 which contracts from 0.3 to 1500 K [7]. NTE has been attributed to the effect of low-frequency rigid unit modes (RUM), that cause rigid rotations of the basic polyhedral units [4, 12].

The discovery of strong NTE materials has also renewed the interest for a deeper basic understanding of the mechanisms at the origin of NTE [6,8,13].

A simple example of framework structure is the cuprite structure shared by Ag_2O and Cu_2O [21], which exhibit NTE in large temperature interval and can be considered as a bridging between the diamond-zincblende structures and the more complex framework structures such as ZrW_2O_8 . The cuprite structure is made up by two interpenetrating lattices, one fcc of metal atoms, "Ag" or "Cu" and one bcc of "O" atoms, each metal atom is linearly coordinated to two "O" atoms, while each "O" atom is tetrahedrally coordinate to four metal atoms.

A comparison between different crystals exhibiting NTE is shown in Fig. (1.2). In Fig. (1.2), two characteristics can be evidenced (a) the great majority of framework structures exhibit NTE within the full temperature interval, Ag_2O has this behavior, indicating that the tension effect always prevails on the stretching effect over the whole temperature range. (b) Cu_2O has the same behavior of zincblende CuCl, the tension effect prevailing only in a limited low-temperature interval, but low-temperature NTE is stronger in CuCl which has a tetrahedral structure (polyhedral rigid units not present). This indicates that a clear connection between the role of polyhedral RUMs and NTE cannot be established for all the framework structures [8,22] but a deeper understanding of NTE could be obtained by a comparative study of framework and zincblende structures.

A common feature of all NTE materials, independent of the presence of polyhedral RUMs, seems to be the influence of strong vibrations perpendicular to the some interatomic bonds, which can be connected to the tension effect.

The applied research on NTE is focused on the search of new substances, the optimization of synthesis procedures and the production of composite materials with specific thermal expansion coefficient tailored to meet specific thermal expansion requirements [1, 5, 20].



Figure 1.2. Relative thermal expansion for some crystals with different structures. The data for CuCl is taken from reference, Cu_2O [20], Ag_2O [20], ZrW_2O_8 [7], $Zn(CN)_2$ [23].

The expansion of materials may be isotropic or anisotropic. In isotropic expansion, the material expands by the same extent in any direction upon heating and this form characterizes the isotropic materials like cubic crystals. In the anisotropic expansion, the extent of expansion is dependent on the particular direction of the material where the measurement is taken.

The macroscopic thermal expansion is measured by conventional techniques such as dilatometry and Bragg diffraction that are sensitive only to the lattice thermal expansion. In the last years, the possibility of obtaining complementary information on the local structure and dynamics from correlation-sensitive probes, such as EXAFS [24] and diffuse scattering [25], has been experimentally demonstrated. EXAFS can give information on the local dynamical behavior of crystals opening new perspectives for understanding the origin of NTE (see section 1.5). A recent and updated review of NTE in a wide range of simple and complex systems can be found in Ref. [6] (and references therein). In this work, we will restrict ourselves to study the NTE due to vibrational effects on simple tetrahedrally bonded crystals.

1.2 Thermodynamic relations

The extent of thermal expansion is measured by the volumetric thermal expansion coefficient β defined as:

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_P \tag{1.1}$$

where ρ is the sample density. The corresponding definition for the coefficient of linear thermal expansion is given by:

$$\alpha_L = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_P \tag{1.2}$$

The practical definitions of β and α_L are often given:

$$\beta = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_P \qquad \alpha_L = \frac{1}{L_0} \left(\frac{\partial L}{\partial T} \right)_P \tag{1.3}$$

where V_0 and L_0 are the room temperature values of V and L.

When the expansion is isotropic, $\beta = 3\alpha_L$. However not all materials expand isotropically, in non-cubic materials the thermal stresses and elasticity are both anisotropic and thermal expansion is related to them. In most cases, the materials expand when heated, i.e. V increases (ρ decreases) or L increases as the T increases with the result that thermal expansion coefficients β or α are positive.

However, some materials contract when heated, in such cases the thermal expansion coefficients β or α_L are negative (α_L may be negative in one direction or more directions).

There are alternative forms of the thermodynamical relations for defining the thermal expansion coefficient of the materials as follow.

Thermal Expansion and Gibbs free energy

It is known that changing the temperature must change the internal pressure and that dimensions will change to minimize the Gibbs free energy G, where G = F(T, V) + PV, F is the Helmholtz energy U - TS, and S is the entropy of the system. Since dG = -SdT + VdP, the volumetric expansion coefficient is given by the second derivative of G as [6]:

$$\beta = \left(\frac{\partial \ln V}{\partial T}\right)_P = \frac{1}{V} \frac{\partial^2 G}{\partial P \partial T} \tag{1.4}$$

In a Cubic or isotropic system, the volume V at temperature T under an applied pressure P_0 is the one that gives the minimum of the Gibbs energy $G = F(T, V) + P_0V$. Fig. (1.3) shows isothermal plots of the free energy G versus V at two different temperatures T and $T + \delta T$ for (a) Positive and (b) Negative thermal expansion. When the temperature increases the system will change its volume to minimize G, in the PTE the change of the volume is positive and hence the system expands but for NTE the volume change is negative and the system contracts.

In Fig. (1.3), one can see that the positive or negative expansion also depends on the "direction" of increasing entropy. For $P = P_0 = \text{Constant}$, dG = -S(V,T)dT. The relation of the volume dependence of the entropy can be obtained, exploiting the Maxwell relationship:

$$\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T,\tag{1.5}$$

so that the volumetric thermal expansion is written as:

$$\beta = -\frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T = \chi_T \left(\frac{\partial S}{\partial V} \right)_T \tag{1.6}$$

where χ_T is the isothermal compressibility $-(\partial V/\partial P)_T/V = -(1/K_T)$, K_T is the isothermal bulk modulus. The compressibility is always positive, then the sign of $(\partial S/\partial V)$ determines the sign of the expansion coefficient, β . Normally, the entropy becomes smaller when increasing pressure say decreasing volume, then β is positive. However, negative β indicates that the entropy increases under increasing the pressure i.e. with decrease in volume.

In Non-cubic systems, a similar treatment can be done by considering the variation of all independent strain coefficient to find the minimum of G [6].



Figure 1.3. Isothermal plots of the Gibss free energy versus volume at constant pressure. (a) for positive thermal expansion and (b) for negative thermal expansion. Figures from ref. [6]

Grüneisen function

Another important thermodynamic relation related to the thermal expansion can be considered using Maxwell relations or equivalently the chain rule:

$$\left(\frac{\partial V}{\partial T}\right)_{P} = -\left(\frac{\partial V}{\partial P}\right)_{T} \left(\frac{\partial P}{\partial T}\right)_{V}$$
(1.7)

Then, we can express β in Eq. (1.1) as:

$$\beta = \chi_T \left(\frac{\partial P}{\partial T}\right)_V = \chi_T \left(\frac{\partial P}{\partial U}\right)_V \cdot \left(\frac{\partial U}{\partial T}\right)_V$$
(1.8)

where, U is the internal energy. In Eq. (1.8), the thermal expansion appears as the elastic response to the thermal stress $(\partial P/\partial T)_V$. Thermal stress coefficient can be expressed as the product of two factors: (i) the heat capacity $C_V = (\partial U/\partial T)_V$ and (ii) the thermodynamic Grüneisen function, $\gamma(T, V) = (\partial P/\partial (U/V))_V$.

Finally, the volumetric thermal expansion coefficient β can be express as:

$$\beta = \chi_T(C_V/V) \left(\frac{\partial P}{\partial (U/V)}\right)_V = \chi_T(C_V/V)\gamma$$
(1.9)

The Grüneisen function γ is dimensionless, χ_T and C_V are both always positive, so γ determines the sign of the expansion, β positive or negative. Experimentally, $\gamma(T, V)$ is usually determined at atmospheric or zero pressure from the measurements of β , χ_S and C_P by means of the expression $\beta V/\chi_S C_P = \beta V/\chi_T C_v$.

The plot of γ against T is often used to display the results of expansion measurements, which have different type behavior for different solids (see Fig. 1.4). It is particularly useful at low temperatures, where both β and C_V can change by many orders of magnitude while γ usually remains of order unity.

1.3 Quasi-Harmonic Approximation

There are different contributions to thermal expansion, here we are interested only on the vibrational contribution and neglect the electronic, magnetic and other contributions which are not appreciable over a wide range of temperature. In all solids



Figure 1.4. The Grüneisen $\gamma(T)$ versus reduced temperature, T/θ_0 (θ_0 the Debye temperature) for crystal of Zincblende structure. The figure is taken from ref. [17].

the atomic vibrations contribute to the heat capacity and thermal expansion. The vibrations are governed by the potential energy ϕ of the crystal. This potential energy can be expressed as a Taylor expansion in the displacements of atoms from their mean positions [17]:

$$\phi = \phi_0 + \phi_1 + \phi_2 + \phi_3 + \phi_4 + \dots \tag{1.10}$$

where ϕ_n is the term of order "n" in the displacements. In the limit of small amplitudes, the vibrations are harmonic and atomic motion can be expressed as a superposition of a set of independent "normal modes" of vibration, each behaving as a linear harmonic oscillator. From Eq.(1.10), the harmonic approximation is considered by neglecting all terms beyond the second order in the displacement [6,17] and the series would terminate at ϕ_2 . The atomic displacement are then symmetric at the equilibrum positions of atoms and the symmetry indicates that there is no thermal expansion. A perfectly harmonic crystal would have frequencies independent of the volume.

The real solids are never purely harmonic and even at the lowest temperatures there

is always some departure from harmonic behavior: "anharmonic effects" are responsible for thermal expansion. When the anharmonicity is weak (vibrational amplitudes are small at low temperatures), anharmonic effects can be calculated by perturbation theory; to the first order the anharmonic potential has two effects [17]: (i) interaction between different normal modes of vibration, (ii) volume dependence of the normal frequencies. The second effect affects the thermodynamic properties giving rise to thermal pressure and hence to thermal expansion. The lowest order terms determining the thermal expansion and related properties are given correctly by the quasi-harmonic approximation which takes into account the dependence of harmonic frequencies on the volume and neglect all other anharmonic effects. Therefore Eq. (1.10) is again limited to the second term ϕ_2 but now the frequencies are volume-dependent.

In quasi Harmonic approximation, the different normal modes are independent of each other and contribute separately to the thermodynamic properties as simple harmonic oscillators. Then the lattice vibrational free energy F_{vib} , entropy S_{vib} and heat capacity C_{vib} are sums of separate contributions f_j , s_j and c_j from different independent vibrational modes of frequency $\omega_j(V)$ and are given as:

• vibrational contribution to the Helmholtz free energy

$$F_{vib} = \sum_{j} \left[\frac{1}{2} \hbar \omega_j + kT \ln(1 - e^{-\hbar \omega_j/kT}) \right]$$
(1.11)

where ω_j is the angular frequency $2\pi\nu_j$ of normal mode j and the first term represents the zero-point energy.

• vibrational contribution to the entropy

$$S_{vib} = \sum_{j} s_j = \sum_{j} s(\hbar\omega_j/kT)$$
(1.12)

• vibrational contribution to the heat capacity

$$C_{vib} = \sum_{j} c_{j} = \sum_{j} c(\hbar \omega_{j}/kT)$$
(1.13)

where c_j is the contribution of mode j to C_V and depends only on $\hbar \omega_j/kT$

• the volume derivatives of the mode frequencies ω_j are conveniently described by dimensionless mode Grüneisen parameters γ_j , defined by [6]:

$$\gamma_j = -\frac{d\ln\omega_j}{d\ln V} = -V\frac{\partial\ln\omega_j}{\partial V} = k_T \frac{\partial\ln\omega_j}{\partial P}$$
(1.14)

The values of Grünesien parameters γ_j can be determined by spectroscopic measurements under pressure, which relates thermal expansion to the volume dependence of spectroscopic frequencies or other characteristic energies. Different vibrations may have different frequencies and different Grünesien parameters, then the thermal pressure coefficient can be rewritten as:

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{V} \sum_j c_j \gamma_j \tag{1.15}$$

From Eqs. (1.14) and (1.15), the total vibrational Grüneisen function becomes the average of the γ_j weighted by the c_j :

$$\gamma = \sum_{j} c_j \gamma_j / \sum_{j} c_j \tag{1.16}$$

Then the vibrational contribution to volumetric expansion coefficient β is given by [6,17]:

$$\beta_{vib} = \frac{\chi_T}{V} \gamma_{vib} C_{vib} = \frac{\chi_T}{V} \sum_j \gamma_j c_j \tag{1.17}$$

where the summation as usual is taken over all normal modes. The thermal expansion will be positive or negative depending upon wether positive or negative γ_j predominate in the weighted average of Eq. (1.16). If the frequency $\omega_j(V)$ of a certain mode decreases with increasing the pressure (or decreasing the volume), then Grünesien parameter γ_j becomes negative (Eq.1.14) and through Eq.(1.17) will contribute negatively to the thermal expansion.

1.4 Vibrational mechanisms in thermal expansion

The vibrations of solids of N atoms are governed by the potential energy which is a 3N-dimensional function of the atomic displacements. The *effective pair potentials* between neighboring atoms are often dominant and have formed the basis for much theoretical work. This pairwise interatomic potential is anharmonic (Fig. 1.1) and is responsible of the thermal expansion. A widespread phenomenological explanation for thermal expansion assumes central forces between pairs of interacting atoms.

1.4.1 Central force mechanisms

The central force between a pair of atoms fluctuates as a consequence of the atomic vibrations and elastic response of the crystal is to restore the mean interatomic distance to its equilibrium value. Corresponding to the pairwise interatomic potential, there are two main vibrational mechanisms contributing with opposite effect to thermal expansion [6] so that the expansion coefficient β will be positive or negative depending upon which effect is larger.

(a) The Bond-stretching effect

The bond stretching mechanism is responsible for the Positive thermal expansion according to two forms of explanation [18]:

(i) Bond stretching mechanism is due to the asymmetry of the effective pair potential when the atoms vibrate along a line connecting the pair as shown in Fig. (1.5). The asymmetry of the potential energy causes the mean interatomic distance to increase with increasing the amplitude of vibrations. We can relate the stretching mechanism to the Grüneisen parameter γ_i ; of a mode j with a component of relative motion along the line joining the two atoms (bond direction). Increasing the volume causes the interatomic bond to lengthen (bond-stretching), so that the force constant affecting the vibrations decreases (weaken the bond) and lowers the mode frequency ω_i , so contributing *positively* to γ_i and to the thermal expansion.

(ii) Another explanation of the stretching mechanism can be equivalently obtained from thermal pressure by considering the term $(\partial P/\partial T)_V$. The repulsive or attractive



Figure 1.5. The bond stretching effect is due to the asymmetry of pair potential which results in a net repulsive force between the two atoms A and B, this contribute positively to the thermal expansion.

force between atoms correspond to distances between atoms r smaller or larger than the equilibrium value r_0 , respectively. At constant volume, the distance r_0 between the atomic mean positions remains fixed; when the atoms vibrate the average force between them will be a net repulsive force, i.e. the magnitude of the repulsion between atoms ($r < r_0$) is greater than that of the attraction ($r > r_0$) (Fig. 1.5). This repulsive force leads to positive thermal pressure and increases with temperature contributing positively to $(\partial P/\partial T)_V$) and then to thermal expansion.

(b) The tension effect

In solids there are also components of relative motion perpendicular (transverse) to the line joining two atoms, these give rise to a second mechanism (Tension effect, also anharmonic) pulling the atoms towards each other and tending to decrease the distance between the average positions of two atoms (Fig. 1.6) and so to contract the solid. The tension mechanism is the earliest vibrational model giving negative thermal expansion [6, 26].

For vibrations with components of relative displacement perpendicular to the bond direction, the mean interatomic distance $\langle r \rangle$ (true bond length) is greater than the distance between the mean atomic positions R_C (apparent bond length). It can be explained in term of Grüneisen parameter γ_i , corresponding to vibrations perpendicular to the line of atomic centers. An increase in volume increases tension in the bonds; then the restoring force for transverse motion is enhanced, raising the frequency and so contributing negatively to γ_i and to thermal expansion.

Equivalently, the tension mechanism can be explained by considering the term $(\partial P/\partial T)_V$. The mean bond length is the time average of the distance between atoms. At constant volume, the distance between mean atomic positions remains fixed, the relative motion transverse to the bond increases the time averaged distance between the atoms, producing net attractive force and hence contributing negatively to $(\partial P/\partial T)_V$ and to thermal expansion.

A further mechanism becomes operative when the relative vibration of two atoms is neither purely along nor purely perpendicular to the bond direction, then stretch-



Figure 1.6. The tension effect: a net attractive force between two atoms A and B is produced from their relative vibrations perpendicular to the bond direction and contribute negatively to thermal expansion.

ing and tension effects contribute simultaneously to the thermal expansion. From the average over a vibrational period, there is a net torque on the atom pair that tends to rotate the bond direction away from the direction of the relative motion [6]. This mechanism is much less important than the above mechanisms because different vibrations try to rotate the bond in different directions and their effects largely cancel. This effect is completely canceled when the bond directions are determined by the crystal symmetry, as in many cubic crystals.

The two different mechanisms (a) and (b), are always important in the interpretation of the crystal vibrations, then central forces play a major role in all crystals. In most crystal vibrations, the displacements have components both along and perpendicular to the line joining neighboring atoms and therefore the two mechanisms occur simultaneously with opposite effects. Usually the bond stretching effect is the largest and thermal expansion is positive. However, when the vibrational modes have large components of relative displacement transverse to bond direction, then the tension effect can predominate and gives rise to negative expansion. These components are generally of low frequency and hence they are low energy transverse acoustic modes. These modes are preferentially excited at low temperatures and are supported by low shear moduli of the material [27], in contrast, most modes favoring the stretching mechanism are not excited until higher temperature. As a consequence γ_{vib} often decreases at low temperature corresponding to the fact that the low frequency transverse "acoustic modes" predominate and are connected to tension effect and give rise to negative thermal expansion.

On the other hand, at high temperature the high energy longitudinal modes are excited and then the stretching effect predominates and hence suppress the NTE [6,28]. The tension effect responsible for NTE is particularly marked for crystals of open structure (the coordination number is small) and with relatively low shear moduli [27].

1.4.2 Non-Central force mechanism

The above considerations can be directly applied when central forces between nearest neighboring atoms (two-body) are dominant. But in the systems with open structures, additional contributions are required for stability, provided by short range non-central forces or by interactions between further neighbors. These non-central forces reduce the tension effect, they resist the vibrations transverse to bond directions.

Therefore, Negative expansion will be favored when such forces are small, even though they are large enough to stabilize the open structure. However, the open structure materials with pronounced NTE are expected to have weak non-central forces and to be close to structural instability [6, 10, 29].

Tetrahedral crystals are stabilized by non-central forces. Relating to the Phillips ionicity factor f_i [30, 31], which is unity when the bonding is purely ionic and zero when it is purely covalent. CuCl is strongly ionic with $f_i = 0.75$ and hence dominated by the central force mechanism, i.e. small non-central forces, where thermal expansion is strongly negative at low temperatures.

In contrast, Ge has $f_i = 0$, with strong stabilizing non-central forces. Then, Negative expansion at low temperatures is reduced and the expansion appears to be positive at nearly all temperatures [32, 33] (for more details see Chapter 3).

1.5 EXAFS studies of the NTE

From a microscopic point of view, the vibrational origin of NTE has been proposed on the basis of simple central force mechanisms [6]. In two-atomic system, the anharmonicity of the pair potential induces positive thermal expansion, via a bond-stretching effect. As we have just seen, geometrical tension effects connected to vibrational motion perpendicular to the bond direction, induce a negative contribution to the thermal expansion, which can in some cases overcome the positive bond-stretching contribution and give rise to NTE. Tension effects can be claimed as origin of NTE in many systems and the deeper quantitative understanding of the microscopic mechanism of NTE requires the availability of accurate experimental information concerning the local behavior around the atoms.

Conventional techniques such as macroscopic dilatometry and Bragg diffraction are sensitive only to the lattice thermal expansion and cannot disentangle the bond stretching from the tension effects. From a microscopic point of view, one is interested in the expansion of the distances between neighboring atoms (nearest-neighbors, nextnearest-neighbors, etc), which will be for short indicated as "bond expansion". From a local perspective, the bond expansion can be distinguished as (i) "true" bond expansion is the variation of the average distances between instantaneous positions $\langle |r_2 - r_1| \rangle$, (ii) "apparent" bond expansion is the variation of the distance between average positions of two atoms $|\langle r_2 \rangle - \langle r_1 \rangle|$. Bragg diffraction measures the "apparent" bond expansion, which is directly connected to the macroscopic expansion.

The measurement of the true expansion of selected bonds and its comparison with the corresponding "apparent" expansion is crucial for understanding the origin of NTE. Actually, the difference between "true" and "apparent" expansions is mainly due to perpendicular vibrations and thus connected to the tension effect. An estimation of the true expansion from Bragg diffraction experiments can be done only in indirect and very approximate way e.g. through the "riding model". The inadequacy of the riding model has been discussed in Ref. [34]. A direct measurement of the true bond expansion is now possible, thanks to investigation tools like total scattering [25] and EXAFS, which rely on the properties of last-generation synchrotron radiation and on refined data analysis procedures.

The analysis of diffuse scattering gives the same sensitivity to correlation as EXAFS analysis; the main strength and limitation of EXAFS technique are related to its selectivity of atomic species and sensitivity to short range order, respectively.

Important advances have been made in the use of EXAFS for thermal expansion studies [35,36] related to; the high accuracy temperature dependent EXAFS measurements and to the approaches which are used in the data analysis. EXAFS (a) directly measures the average value of the instantaneous distance between neighboring atoms and its thermal expansion, " true bond expansion". (b) gives directly the mean square relative displacement along the direction of the bond (parallel MSRD).

The average distance $\langle r \rangle$ measured by EXAFS is larger than the distance R_c between the average positions measured by diffraction because of the vibrations perpendicular to the bond. Correspondingly larger is also the thermal expansion measured by EXAFS. From the difference between the expansions $\delta \langle r \rangle$ and δR_c measured by EX-AFS and diffraction, respectively, one can get information on the relative vibrations in the plane perpendicular to the bond (Perpendicular MSRD). Therefore, EXAFS can give original information, complementary to Bragg diffraction, on the local mechanisms responsible for NTE.

The accuracy and reliability of the bond thermal expansions and of both parallel and perpendicular MSRDs, obtainable from EXAFS has been checked by measuring high-quality spectra of simple model systems, such as Cu [24] and Ge [36], analyzing them by the cumulant expansion approach and comparing the results with theoretical calculations [37]. From the MSRDs measured by EXAFS (a) the anisotropy of the relative vibration i.e. parallel to perpendicular MSRDs can be calculated and connected to the tension effect giving rise to NTE. (b) From the comparison with the MSDs measured by diffraction, one can give original information on the relative phase of vibration of the atoms.

To evaluate the potential of EXAFS for NTE studies, several crystals with different structures (diamond-zincblende, cuprite and delafossite) and affected by different NTE properties have been investigated [14, 22, 34, 36, 38]. To evaluate strengths and limitations of EXAFS for quantitative studies of NTE materials, it is convenient now to focus the attention on crystals of relatively simple structure and lattice dynamical properties, such as tetrahedrally bonded semiconductor with the diamond-zincblende structure.

Recently, from EXAFS studies on Ge and CuCl crystals, the results suggested the existence of a well defined correlation between the NTE properties and some quantities measured by EXAFS. To confirm this correlation and looking for its quantitative assessment, EXAFS studies have been performed on the CdTe, whose NTE properties are intermediate between them.

Chapter 2

EXAFS and Thermal properties

X-ray Absorption Fine Structure (XAFS) is a powerful technique for studying the local properties (structural, thermal and electronic) of materials in chemistry, physics, biology and other fields. During the last two decades, the use of XAFS has become firmly established as a practical and powerful analytical technique for structure determination.

2.1 EXAFS technique

EXAFS (Extended X-ray Absorption Fine Structure) is based on studying the absorption of x-ray photons by the material under study as a function of photon energy. The observed EXAFS signal is the modulation of the X-ray absorption coefficient as a function of X-ray energy.

From the discovery of EXAFS phenomenon in 1920s until 1970s, the basic mechanism had been understood but the quantitative theory as well as comprehensive rate analysis of EXAFS measurements was lacking. Thanks to the availability of synchrotron sources [39] and the development of a suitable interpretation scheme, become it possible to exploit XAFS signal to get information on both the local geometric and electronic structure of matter. EXAFS provides information on the nearest coordination shells to the absorbing atom and hence the Short-Range order theory is the suitable theory for EXAFS interpretation [40]. EXAFS is particularly suited to study the thermal properties within a few coordination shells of a selected atomic species by performing temperature dependent its measurement.

2.1.1 Introduction

In the interaction of the x-rays with matter, several different physical processes can occur at a microscopic level as shown in Fig. (2.1). For energies below 1 MeV the two basic interactions are photoelectric absorption and x-ray scattering which have a different cross section which depends on the photon energy. In the photoelectric absorption process (Fig. 2.1); an X-ray photon is absorbed by core electron leading to either the excitation or ionization of the atom, according to weather the photon energy is lower or larger than the electron binding energy, respectively. In X-ray scattering process; the path of the X-ray photon is deflected after scattering by an electron, which can be either coherent (i.e. the elastic Thomson scattering) or incoherent (i.e. the inelastic Compton scattering).

Actually, these two processes represent the origin of a lot of experimental techniques. Here we are interested in the photoelectric absorption process which is the origin of the X-ray Absorption Fine Structure (XAFS) technique. In the X-ray absorption process we are concerned with the absorption coefficient $\mu(E)$ which gives the probability that X-rays will be absorbed when passing through a sample of thickness x according to Beer's law:

$$I = I_0 e^{-\mu(E)x}$$
(2.1)

where I_0 and I are the incident and transmitted X-ray intensity through the sample, respectively. I will be decreased by an amount that is determined by the absorption characteristics of the sample, the I_0 intensity is proportional to the number of X-ray photons.

At most X-ray energies, the absorption coefficient $\mu(E)$ is a smooth function of energy


Figure 2.1. The photoelectric process(Left): The interaction of X-rays with matter and the corresponding partial cross sections of the different processes can be occur during the interaction(Right).

(Fig. 2.1) with a value given by [41, 42]:

$$\mu(E) \approx \frac{\rho Z^4}{AE^3} \tag{2.2}$$

where ρ is the sample density, E the X-ray energy, Z the atomic number and A the atomic mass. The strong dependence of $\mu(E)$ on the atomic number Z and E (Fig. 2.3) is a fundamental property of x-rays that makes x-ray absorption useful in medical and other imaging technique.

Following the absorption event, the atom is left in an excited state with an empty electronic level (a core hole), this excited state will eventually decay (De-excitation process) typically within a few femtoseconds. The excited core hole will relax back to a ground state of the atom; a higher level core electron drops into the core hole and a fluorescence x-ray or Auger electron is emitted as shown in Fig. (2.2).

In both cases the probability of emission (X-ray or electron) is directly proportional to the absorption probability and occurs at discrete energies that are characteristic of the absorbing atom, and can be used to identify the absorbing atom.



Figure 2.2. competing decay processes following the presence of the core hole: Radiative transition, X-ray fluorescence (up) and non radiative transition, Auger effect Decay (down) of the excited state.

2.1.2 XAFS: X-ray Absorption Fine Structure

XAFS is the modulation of the X-ray absorption coefficient at energies near and above an X-ray absorption edge. XAFS measures the energy dependence of μ at and above the binding energy of core-electron of a given atomic species.

Absorption edge

The X-ray absorption spectrum exhibits a generally smooth decreasing intensity to higher energy, increasing the energy of the incident X-ray photons leads to a progressive monotonic decrease in the X-ray absorption coefficient μ [43]. The smooth behavior of the photo-electric coefficient is interrupted by sharp discontinuities called X-ray absorption edges (Fig. 2.3, left). The absorption edge is originated when the X-ray photon energy is high enough to extract an electron from a deeper core level to the continuum.

There are different absorption edges for each element corresponding to which energy level the electrons were extracted from: K, L₁, L₂, L₃ and M₁-edges corresponds to the extraction of an electron from the energy levels 1s, 2s, $2p_{1/2}$, $2p_{3/2}$ and 3s respectively as shown in Fig. (2.3, right).



Figure 2.3. X-ray absorption edges corresponding to different core energy level.

The energy of an absorption edge depends on the binding energy of the corresponding core energy level. Since the binding energies grow monotonically with the atomic number Z [41, 42] (Fig. 2.4), every edge energy corresponds to a well defined atomic species. Every atomic species has one K edge (highest energy absorption edges), whose energy grows with the atomic number Z, from 13.6 eV for hydrogen to 115.606 keV for Uranium.

At the absorption edge E_{edge} the kinetic energy of the electron E_k is defined to be equal to E_0 often referred to as the zero-point energy or "inner potential". For any energy above this, the photoelectron kinetic energy is given by:

$$E_k = h\nu - E_{binding} \tag{2.3}$$

Fine Structure

Above an absorption edge, the X-ray absorption coefficient exhibits some fine oscillations is called X-ray Absorption Fine Structure XAFS [43, 44]. Therefore, in XAFS measurements we are concerned to measure the intensity of μ as a function of energy near and above the absorption edges. The range of the XAFS region depends on the material under investigation, and is strongly influenced by the presence of atoms surrounding the absorber atom. For isolated atoms (i.e noble gases, metallic vapors),



Figure 2.4. Left: The absorption cross section μ/ρ for several elements over the x-ray energy range of 1 to 100 keV. Right: Binding energy of electrons in some core levels as a function of the atomic number Z.

XAFS region is limited to a few eV around the edge, while for the molecular gases and condensed systems, XAFS region can extend up to 1000 eV above the edge. In this case, the fine structure is indeed "defined" by the atoms which surround the atomic species being excited.

The XAFS region is generally regarded as the total of two subregions as shown in Fig. (2.5):

- X-ray Absorption Near Edge structure (XANES), typically within 30-50 eV above the absorption edge, which contains information on the local electronic and geometric structure [44, 45].
- Extend X-ray Absorption Fine Structure (EXAFS), which approximately starts after the XANES region and extends up to typically 1000 eV. EXAFS region carries information on the local geometric structure surrounding a given atomic species.

Actually the limits of the energy ranges of the EXAFS and XANES regions are not so well defined, and depends on the case under study. XANES is strongly sensitive to chemical valence and coordination chemistry of the absorbing atom, while EXAFS is



Figure 2.5. The XANES and EXAFS regions are schematically illustrated at the Ge K-edge.

used to determined the distances, coordination number and species of the neighbors of the absorbing atom.

2.1.3 The EXAFS mechanism

A simple phenomenological picture is often used to describe the origin of EXAFS as shown in Fig. (2.7). When an X-ray photon of sufficiently high energy is absorbed by an atom, a core electron (photoelectron) is ejected from the atom, and the atom becomes ionized (ionization process). The outgoing photo-electron is described by a wave function approximated by a spherical wave.

If the absorber atom is isolated, the $\mu(E)$ has a sharp step at the core level binding energy and features a smooth function above this absorption edge as shown in Fig. (2.6). For a cluster of atoms, the absorbing atom is surrounded by neighboring atoms, the outgoing photoelectron spherical wave will be backscattered by the surrounding atoms, giving rise to an incoming spherical wave. In this case, the x-ray absorption coefficient of the sample will depends on the superposition of these outgoing and incoming waves of the photoelectron (Fig. 2.7).



Figure 2.6. X-ray absorption by a free atom and the corresponding absorption spectrum if the absorber atom is isolated

The phase relationship between outgoing and incoming waves depends on photoelectron wavelength and interatomic distance between absorber and backscatter atom. The EXAFS oscillations as a function of the photoelectron wavelength may be interpreted as due to the interference between outgoing and incoming waves. The interference phenomenon can indeed monitor the local structure around the absorber atom.

Actually, the interpretation of EXAFS requires a full quantum mechanical treatment based on the time dependent perturbation theory, which is related to the description of the time sequence of events: photon absorption, photoelectron emission, backscattering and interference. The theory describes the absorption coefficient as a transition between two quantum state; the initial core state $_i$ and the photoelectron final state $_f$, which in turn is a superposition of the outgoing and incoming spherical waves.

The back-scattered photoelectron experiences a phase change producing an interference phenomenon. Therefore, the absorption coefficient exhibits producing fine structure because the final wave state function is modulated due to the interference pattern



Figure 2.7. Absorption of cluster of atoms, superposition of the emitted and backscattered photoelectron waves. the absorption increase and decrease according to the constructive and destructive interference respectively.

and can be defined by the equation:

$$\mu(E) = \mu_0(E)[1 + \chi(E)]$$

where $\chi(E)$ forms the oscillatory part of the total absorption coefficient above the absorption edge. The EXAFS function is defined as:

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)}$$
(2.4)

where $\mu(E)$ is the measured absorption coefficient and $\mu_0(E)$ is the atomic absorption coefficient. The experimental determination of μ_0 is difficult, and hence it is usually reproduced by a smooth polynomial function as shown in Fig. (2.8). The division by the edge step $\Delta \mu_0$ corresponds to obtaining the oscillations normalized only to one absorption event. Science the oscillatory part is created by the interference between the outgoing and backscattered waves, therefore $\chi(E)$ contains information about local structure around the absorber atom.

EXAFS oscillations depend strongly on the surrounding atoms of the absorber atom. The frequency of these oscillations depends on the distances between absorber and backscatter atoms (i.e the interatomic distance, R). Their amplitude depends on the number of backscattered atoms (i.e. Coordination number, N). According to these considerations some peculiarities characterize EXAFS as follow:



Figure 2.8. Absorption coefficient and edge jumb.

- the selectivity of atomic species, achieved by tuning the x-ray energy to the corresponding absorption edge.
- Sensitivity to Short-Range Order(SRO) around the absorber atom due to both the spherical nature of the photoelectron wave and short mean free path of the photoelectron.
- Insensitivity to Long-Range Order(LRO).

From these peculiarities, we can realize that EXAFS and X-ray diffraction techniques gives different information but complete each other.

2.2 EXAFS equation

Let us consider only ideal systems composed by atoms frozen at their equilibrium positions [46], the effect of thermal disorder will be introduced later. The oscillation part in the X-ray absorption coefficient of a material contains information on the local structure around the absorber atom and we need to extract this information. Several authors have given derivations for the EXAFS theory [40,47–49]. We will give a short introduction to the EXAFS equation, more detailed derivation can be found in Ref. [46].

The EXAFS function $\chi(k)$ can be estimated in the frame of first-order time dependent perturbation theory assuming some approximations [50]:

- one-electron approximation: only one core electron changes its state, the remaining N-1 electrons (passive electrons) simply relax their orbital around the core hole. Passive electron effects are anyway considered in our formalism by taking into account the effect of their relaxation in the presence of the core hole, and the inelastic interaction between the excited electron and the others.
- Dipole approximation: only the electronic transitions that satisfy the selection rule $\Delta L = \pm 1$ are allowed. the dipole approximation is only valid when the wave length of the photoelectron is much larger than the size of the absorbing atom.
- Single Scattering (SS) approximation: the multiple scattering (MS) contributions are neglected, and only the single backscattering events from the neighboring atoms are considered. In EXAFS region the MS events are less important but sometimes are not negligible. In the 1 st-shell there is only SS contribution, so the signal can be safely analyzed within the SS approximation, where MS paths corresponds to longer effective distance.
- Plane wave approximation; The curvature of the spherical wave impinging on the scattering atom is neglected (small atom approximation)

EXAFS oscillation is due to the coherent superposition of the outgoing and incoming spherical waves of only one photoelectron as shown in Fig. (2.9). The absorption coefficient μ is proportional to the transition probability per unit time of the photoelectron event and from Fermi's Golden Rule (2.5), the absorption coefficient is given by:

$$\mu = \frac{4\pi^2 e^2 \omega N_A}{c} |\langle i | \hat{\eta}. \bar{r} | f \rangle|^2 \rho(E_f)$$
(2.5)

Where ω is X-ray frequency, N_A the atomic density, $\rho(E_f)$ is the density of final electronic state and $\langle i | \hat{\eta}.\bar{r} | f \rangle$ is the matrix element for the transition from the initial



Figure 2.9. Schematic illustration of the EXAFS mechanism showing the interference between the incoming and outgoing photoelectron spherical waves.

state $|i\rangle$ of energy E_i to the final state $|f\rangle$ of energy $E_f = E_i + \hbar\omega$ [51]. EXAFS oscillations are entirely described by the matrix element $|\langle i | \hat{\eta}.\bar{r} | f \rangle|^2$ in which:

- $\langle i|$: the initial-state describes core electron (is not influenced by the neighboring atom).
- |f>: the final-state describes the photoelectron (influenced by the neighboring atom)

In the EXAFS region the final density of electron states $\rho(E_f)$ is constant, then Eq. (2.5) can be written as:

$$\mu = C \left| \langle i | \hat{\eta}. \bar{r} | f \rangle \right|^2 \tag{2.6}$$

where C is a constant. If the absorber atom is isolated (see Fig. 2.6), the final state of the photoelectron can be described by an undisturbed outgoing spherical wave and the absorption coefficient is given by:

$$\mu_0 = C \left| \langle i | \hat{\eta}. \bar{r} | f_0 \rangle \right|^2 \tag{2.7}$$

where $\mu_0(E)$ is called atomic absorption coefficient and decreases monotonically as a function of the photon energy $\hbar\omega$.

If the absorber atom is not isolated (see Fig.2.9), the outgoing photoelectron spherical

waves back-scattered by the surrounding atoms induce weak perturbation δf (photoelectron energy is much larger than the electron-atom interaction) to the final state $|f\rangle = |f_0\rangle + |\delta f\rangle$ and the absorption coefficient becomes:

$$\mu = C |\langle i | \hat{\eta}.\bar{r} | f_0 + \delta f \rangle|^2$$
(2.8)

Phenomenologically the perturbation δf corresponds to an incoming spherical wave (backscattered photoelectron waves) which modifies the superposition integral of the final state $\langle f |$ with the initial state $\langle i |$ in the matrix element in Eq. (2.8) with respect to equation (2.7).

By expanding the absorption coefficient in Eq. (2.8) and neglecting the second order terms in δf , we obtain:

$$\mu = C \left[|\langle i | \hat{\eta}.\bar{r} | f_0 \rangle|^2 + 2Re \langle i | \hat{\eta}.\bar{r} | f_0 \rangle \langle i | \hat{\eta}.\bar{r} | \delta f \rangle^* \right]$$
(2.9)

The EXAFS function is generally expressed as a function of the photoelectron wave number k rather than the energy and given by:

$$\chi(k) = \frac{\mu - \mu_0}{\mu_0} \tag{2.10}$$

where the photoelectron wave vector k is given by:

$$k = \sqrt{\frac{2m}{\hbar^2}(E - E_b)} \tag{2.11}$$

By inserting the absorption coefficients, Eqs. (2.7) and (2.9) in EXAFS function (2.10) we obtain:

$$\chi(k) = 2Re\left(\frac{\langle i|\hat{\eta}.\,\bar{r}|\delta f\rangle^*}{\langle i|\hat{\eta}.\,\bar{r}|f_0\rangle}\right)$$
(2.12)

It is important to understand the perturbation δf developed along the photoelectron path in order to calculate EXAFS Eq. (2.12).

Two-atomic system

The simpler system consists of two atoms, the absorber (A) and the backscatter (B) and R_B is the vector joining the two atomic positions. The photoelectron potential between absorber and backscatter atom is generally treated within the muffin tin approximation, according to which the space is divided into three regions:



Figure 2.10. Schematic representation of the scattering process of the photoelectron wave leaves the absorbing atom A and back-scattered by the surrounding atom B.

- I : spherically symetric potential centered on atom A.
- II : spherically symetric potential centered on atom B.
- III : constant inner potential, connected to the potentials of regions I and II.

We can build up a simple model of EXAFS for two atoms as in Fig. (2.9) to define the perturbation δf developed along the photoelectron path. We describe the outgoing photoelectron wave function traveling as a spherical wave (e^{ikr}/kr) a distance R_B to the neighboring atom (B), then scattering from the atom (B), and traveling as a spherical wave a distance R_B back to the absorbing atom (A) as shown in Fig. (2.10).

According to the scattering theory in plane wave approximation; the scattering process can be described by the partial wave expansion of the plane wave, one can express δf as:

$$\left|\delta f\right\rangle = i \left|f_{0}\right\rangle \frac{\left|f(k,\pi)\right|}{2kR_{B}^{2}} e^{i(2kR_{B}+\Psi+2\delta)}$$

$$(2.13)$$

where



Figure 2.11. The phase shift and backscattering amplitude as a function of wave vector, k for some selected elements.

• $|f(k,\pi)|$ is the complex back-scattering amplitude given by neighboring atom, where expressed as a function of the partial wave phase shifts δ_l as:

$$|f(k,\pi)| = (1/k) \sum_{l=0}^{\infty} (-1)^l (2l+1) e^{i\delta_l} \sin\delta_l$$

- $\Psi(k,\pi)$ is the phase shift of the backscattered photoelectron wave caused by the scattering atom.
- $2\delta(k)$ is the further phase shift due to the potential of the absorbing atom. the factor 2 is due to the fact that the photoelectron interacts twice with this potential

Substituting Eq. (2.13) into Eq.(2.12), one obtains the expression for the EXAFS signal as:

$$\chi(k) = \frac{1}{kR_B^2} |f(k,\pi)| \sin[2kR_B + \phi(k)]$$
(2.14)

With $\phi(k) = \Psi + 2\delta$, where f(k) and $\phi(k)$ are the amplitude and phase shift given by the backscattered photoelectron and called the backscattering amplitude and phase shift, respectively. f(k) and $\phi(k)$ are scattering properties of the neighboring atom which depend on Z as shown in Fig. (2.11). This makes EXAFS sensitive to the atomic species of the neighboring atom. Basically, the EXAFS signal (Eq. 2.14) has a sinusoidal behavior with frequency $2R_B$ proportional to the interatomic distance. The phase of this wave is perturbed by the phase shift $\phi(k)$, while the amplitude is modulated by $|f(k,\pi)|$. The single electron approximation [44] is one of the important approximation in Eq. (2.14), within this approximation the inelastic effects due to many body excitations are negligible.

2.2.1 Many body effects

Referring to the many body interactions, EXAFS Eq. (2.14) should be corrected to take into account the inelastic effects. There are two types of inelastic effects, Intrinsic and Extrinsic within and outside the absorber atom, respectively.

• Intrinsic inelastic effect:

In Eq. (2.14) we did not account for the multiple excitations within the absorber atom itself. This effect gives rise to an inelastic part in the X-ray absorption coefficient. The multiple excitations necessarily modify the energy of the photoelectron, and therefore modify the interference conditions between the outgoing and the incoming waves. The net effect is a reduction of the coherent EXAFS signal with respect to elastic excitations. The fraction of total absorption giving rise to elastic excitations is measured by the superposition factor $S_0^2 = |\langle i^{N-1} | f^{N-1} \rangle|^2$ and its value is generally between 0.7 and 0.9 [44] ($S_0^2 = 1$ when we neglect the multiple excitation effect).

• Extrinsic inelastic effects:

The EXAFS Eq. (2.14) was derived assuming that the outgoing photoelectron went out as a spherical wave (e^{ikr}/kr) . However, we neglect the fact that the photoelectron can also scatter inelastically and may not be able to come back to the absorbing atom. In order to participate to the EXAFS signal, the photoelectron has to scatter from the neighboring atom and return to the absorbing atom elastically (i.e. at the same energy) as the outgoing photoelectron. In addition, the photoelectron has to come back to the absorbing atom before the excited state decays (i.e., before the core-hole is filled). To



Figure 2.12. The photoelectron mean free path $\lambda(k)$ for EXAFS, which includes both the inelastic scattering of the photoelectron and the effect of the finite lifetime of the core-hole.

account for both extrinsic inelastic effects and core-hole lifetime, the spherical wave is damped by factor $e^{-2r/\lambda}$, where $\lambda(k)$ is the photoelectron Mean Free Path (MFP), that measures how far it typically travels before scattering inelastically and/or before the core-hole is filled.

Therefore, EXAFS Eq. (2.14) with taking into account the inelastic effect is given as:

$$\chi(k) = \frac{S_0^2}{kR_B^2} e^{-2R_B/\lambda} |f(k,\pi)| \sin[2kR_B + \phi(k)]$$
(2.15)

In Eq. (2.15), the mean free path $\lambda(k)$ depends on the k range as shown in Fig. (2.12), and progressively reduces the amplitude of EXAFS oscillations when R_B increases. From Fig. (2.12), $\lambda(k)$ for EXAFS is less than 25Å and together with the presence of the term R_B^{-2} , it contributes to make EXAFS insensitive to long range order. This reason explains why EXAFS technique is described as a local structure probe, not able to see much further few Angstroms from the absorbing atom, i.e. sensitive only to short range order .

Many-atomic system

Crystals or poly atomic molecules constitute a "many-atomic" system. Within the single scattering approximation the generalization of Eq. (2.15) is immediate: EXAFS function can be built up as the sum of many-atomic contributions and R is the vector position of the surrounding atoms with respect to absorber atom. For a given shell, EXAFS Eq. (2.15) becomes:

$$\chi(k) = \frac{NS_0^2}{kR^2} e^{-2R/\lambda} |f(k,\pi)| \sin[2kR + \phi(k)]$$
(2.16)

In real systems, there are many coordination shells at different distances and composed of different atom types. Therefore, EXAFS is a sum of the contributions from each coordination shell and given by:

$$\chi(k) = \frac{S_0^2}{k} \sum_j \frac{N_j}{R_j^2} e^{-2R_j/\lambda} |f_j(k,\pi)| \sin[2kR_j + \phi_j(k)]$$
(2.17)

where j represents the individual coordination shell, each one containing N_j atoms approximately at the same distance R_j from the absorber atom.

2.2.2 Thermal disorder effects

EXAFS Eq. (2.17) has been obtained considering the atoms frozen at their eqilibrum positions and completely neglecting the thermal and structural disorder. But every real physical system is affected by thermal disorder, due to the thermal motion of atoms, whose amplitude increases with temperature and is not negligible even at zero degree.

The period of the atomic vibrations ($\simeq 10^{-12}$) is much larger than the photoelectron time of flight ($10^{-16} \div 10^{-15}$ s), thus an EXAFS spectrum, resulting from the contributions of a large number of photoelectrons, samples a distribution $\rho(r)$ of instantaneous interatomic distance r for each coordination shell spread out by the thermal disorder. This disorder reduces the EXAFS intensity. In harmonic approximation, it is taken into account by a factor ($e^{-2k^2\sigma^2}$) (Debye-Waller factor), where σ^2 corresponds to the variance of the distance distribution. When static disorder is also present, the disorder σ^2 is the sum of static(σ_s^2) and thermal (σ_t^2) contributions.

Taking into account all theses effects, the EXAFS Eq. (2.16) can be written as:

$$\chi(k) = \frac{NS_0^2}{kR^2} e^{-2R/\lambda} e^{-2k^2\sigma^2} |f(k,\pi)| \sin[2kR + \phi(k)]$$
(2.18)

In EXAFS Eq. (2.18) for a single coordination shell; having accurate values for the scattering amplitude $f(k, \pi)$, $\lambda(k)$, S_0^2 and phase-shifts $\phi(k)$ (we can extract the following structural parameter:

- R: Average interatomic distance
- N: Coordination number
- σ^2 : Debye-Waller factor

It is important to mention that Eq. (2.18) is a valid approximation only for weak disorder, where the distribution of distances can be assumed to be Gaussian. For the strong disorder, Eq.(2.18) fails to model EXAFS spectra, and more parameters are needed to account for the deviation from the Gaussian approximation.

Let us now introduce the effect of thermal disorder beyond the Harmonic approximation [46] considering only coordination shells containing one atomic species: Due to thermal (and possibly structural) disorder, the distance between absorber and backscatter atoms varies according to a probability distribution $\rho(r)$. The EXAFS signal can be expressed for one coordination shell as [44]:

$$\chi_j(k) = (S_0^2/k) N_j |f_j(\pi, k)| Im \left[e^{i\phi_i} \int_0^\infty \rho(r) \frac{e^{-2r/\lambda}}{r^2} e^{2ikr} dr \right]$$
(2.19)

Eq. (2.19) can be extended also to multiple scattering paths, on the basis of the approach developed by Rehr and co-workers and implemented in the FEFF code [52]. The distribution $\rho(r)$ is commonly referred to as real distribution but the integration in equation (2.19) is the Fourier transform an effective distribution P(r) [9]:

$$P(r,\lambda) = \rho(r) \frac{e^{-2r/\lambda}}{r^2}$$
(2.20)

 $P(r, \lambda)$ is the distribution probed by EXAFS and differs from the real distribution due to the progressive attenuation of the photoelectron spherical wave and to the limited mean free path.

The fundamental problem of EXAFS analysis is to recover the distribution $P(r, \lambda)$ and hence $\rho(r)$ from the experimental spectrum $\chi(k)$. No exact solution can be given to this problem, because every experimental spectrum does not corresponds to full characteristic function but has a finite extension within the k_{min} and k_{max} values. Particularly, for $k_{min} \leq 2 \div 3$ Å⁻¹ the EXAFS signal generally cannot be utilized, due to:

- (i) difficulty in determining the atomic absorption coefficient μ_0 in the vicinity of the edge.
- (ii) effects of the core-hole lifetime on the low-energy electrons.
- (iii) influence of multiple scattering processes.

An approximate solution consists in hypothesizing a physically sound distribution and in fitting its parameters to the experimental EXAFS spectrum [53]. An alternative approach is based on the cumulant method [9,10], which is currently used for systems characterized by not too high levels of disorder.

2.2.3 Cumulant expansion of EXAFS

The integral in Eq. (2.19) is the Fourier transform of the effective distribution $P(r, \lambda)$ or, in the probability terminology, is its characteristic function [54]. This characteristic function is a complex function of a complex variable; its full knowledge is equivalent to the knowledge of the distribution $P(r, \lambda)$.

A characteristic function can be expand as the exponent of a Mac Laurin series around k = 0 given as:

$$\int_0^\infty P(r,\lambda) \exp^{2ikr} dr = \exp\left[\sum_{n=0}^{+\infty} \frac{(2ik)^n C_n}{n!}\right]$$
(2.21)

Where the expansion coefficients C_n are called cumulants. The convergence interval of the cumulant series in Eq. (2.21) depends on the peculiarities of the distribution $P(r, \lambda)$. The cumulants C_n are directly related with the moments of the effective distribution. At low temperatures, materials are characterized by limited thermal disorder, and the harmonic approximation is sound [16].

The lowest order cumulants have a simple interpretation: C_0 depends on the normalization of the distribution, C_1 is the mean value of the distribution, C_2 is the variance, C_3 measures the distribution asymmetry and C_4 measures the flatness of the distribution.

In the harmonic approximation, the distribution is gaussian and the cumulants C_n are zero for n > 2. As the temperature increases, the anharmonic effects becomes important, the distribution will deviate from a Gaussian shape and the higher order cumulants become important. By inserting Eq. (2.21) into Eq. (2.19), EXAFS equation as a function of cumulants [9,44] is given by:

$$\chi_j(k) = (S_0^2/k)N_j |f_j(k,\pi)| \exp\left[C_0 - 2k^2C_2 + \frac{2}{3}k^4C_4 - \dots\right] \sin\left[2kC_1 - \frac{4}{3}k^3C_3 + \dots + \phi_i\right]$$
(2.22)

Phase and amplitude of the EXAFS signal are determined by the odd and even cumulants, respectively. The power of this expansion is the possibility that the odd and even cumulants be studied separately, if phase and amplitude of the EXAFS signal can be disentangled.

The effective distribution is not normalized to one; the normalization factor can be approximated by the relation $e^{C_0} = e^{-2C_1/\lambda}/C_1^2$.

In Eq. (2.22), contains the cumulants C_n of the effective distribution $P(r, \lambda)$, while one is interested in the cumulants C_n^* of the real distribution $\rho(r)$. The connection between the cumulants of the effective and real distribution has been developed [10] and the expression for the first cumulants has been derived by Freund et al. [55] and given by:

$$C_1^* \cong C_1 + \frac{2C_2}{C_1} \left(1 + \frac{C_1}{\lambda} \right)$$
 (2.23)

The difference between the first cumulants C_1 and C_1^* cannot be neglected and now is commonly taken into account in the data analysis for accurate works.

An approximate general relation connecting the cumulants of the real and effective distribution has been derived by M. Vaccari [38, 56], and given by:

$$C_n^* \sim C_n + 2C_{n+1} \left(\frac{1}{C_1} + \frac{1}{\lambda}\right) \qquad n = 1, 2, 3$$
 (2.24)

The first cumulant of the effective distribution is systematically smaller than the first cumulant of the real distribution, as a consequence of the spherical nature of the photoelectron wave and its limited mean free path [55] and this difference can not be neglected. The relative values with respect to a reference at very low temperature of the cumulants were also given by [38, 56]:

$$\delta C_n^* \sim \delta C_n + 2\delta C_{n+1} \left(\frac{1}{R} + \frac{1}{\lambda}\right) \qquad n = 1, 2, 3 \tag{2.25}$$

The differences between the second and higher order cumulants of the two distributions is generally neglected but in some cases can be important. According to the initial moments of real distribution, the cumulants can be interpreted in term of properties of this distribution [9, 10]

• $C_1^* = \langle r \rangle$

First cumulant is the mean value of the distribution

• $C_2^* = \langle (r - \langle r \rangle)^2 \rangle$

Second cumulant is the variance of the distribution

• $C_3^* = \langle (r - \langle r \rangle)^3 \rangle$

Third cumulant measures the distribution asymmetry

• $C_4^* = \langle (r - \langle r \rangle)^4 \rangle$ - 3 μ_2^2 , where $\mu_2 = C_2^*$ (variance) Fourth cumulant measures the flatness of the distribution with respect to gaussian one

In Gaussian distribution, the Cumulants C_n are zero for n > 2.

2.3 EXAFS and local dynamics

To better understand the meaning of EXAFS cumulants C_n^* of the real distribution of distances $\rho(r,T)$, it is useful to investigate their relations with the dynamical properties of the crystals and how to obtain from EXAFS original information on vibrational dynamics and thermal properties.

For systems affected by disorder of only thermal origin, the cumulants can be connected to the local dynamical behavior of the system, i.e to atomic relative displacements both parallel and perpendicular to the interatomic bond.

Let us consider two atoms (absorber and backscatter) of a crystal and R_c be the equilibrium distance between the mean positions of the two atoms. Let r be the instantaneous inter-atomic distance and the interaction between the two atoms is described by an effective potential $V_{eff}(r)$, with the minimum at $r = R_c$. In the classical approximation, the distribution $\rho(r)$ connected to an effective pair potential V_{eff} [10] by:

$$\rho(r,T) = e^{-\beta V_{eff}(r)} \left[\int e^{-\beta V_{eff}(r)} dr \right]^{-1}$$
(2.26)

Let, u_1 and u_2 be the instantaneous thermal displacements of these two atoms from their equilibrium positions as shown in Fig. (2.13, Left) An EXAFS photoelectron samples the modulus of the instantaneous interatomic distance r between absorber and backscatter atoms as given by:

$$r \equiv |r| = |R_c + \Delta u| = \sqrt{(R_c + \Delta u)^2} = R_c \sqrt{1 + 2R_c \cdot \frac{\Delta u}{R_c} + \frac{(\Delta u)^2}{R_c^2}}$$
(2.27)

where $\Delta u = u_1 - u_0$ the relative thermal displacement and can be decomposed into the projections of the relative displacement parallel to the bond direction and in the perpendicular plane respectively, as in Fig. (2.13, Right):

$$\Delta u^2 = \Delta u_{\parallel}^2 + \Delta u_{\perp}^2 \tag{2.28}$$

where $\Delta u_{\parallel} = \hat{R}_c$. Δu and $\Delta u_{\perp} = (\Delta u - \Delta u_{\parallel})^{1/2}$. By decomposing the projections of the relative displacements into Eq. (2.27), an analytical relation for r is given by [57]:

$$r = R_c + \Delta u_{\parallel} + \frac{\Delta u_{\perp}^2}{2R_c} - \frac{\Delta u_{\parallel} (\Delta u_{\perp})^2}{2R_c^2} + \dots$$
(2.29)



Figure 2.13. The thermal ellipsoids of the absorber and backscatter atom. Left: thermal displacements of two atoms from their equilibrium positions. Right: The projections of the relative displacement parallel and perpendicular to the bond direction.

This approximate relation for r has been obtained through Taylor expansion, which considered the small relative displacements with respect to the interatomic distance $x = |\Delta u| / R_c \ll 1.$

The effective pair potential $V_{eff}(r)$ between absorber and backscatter atom can be expressed as a function of the displacement $x = r - R_c$ along the bond direction. In this case, $V_{eff}(r)$ can be expanded as a power series with respect to x and given as:

$$V_{eff}(x) \simeq \frac{1}{2}k_0 x^2 + k_3 x^3 + k_4 x^4 \dots$$
 (2.30)

Here k_0 is the second order (harmonic) force constant, while $k_3, k_4, ...$ are higher order (anharmonic) force constant. In the harmonic approximation, Eq. (2.30) will expand only to the second order term.

2.3.1 Cumulants and lattice dynamics

As we know, the first three cumulants C_i^* represent average value, variance and asymmetry of the EXAFS one dimensional distribution of distances $\rho(r)$. We will separately consider the harmonic approximation and the effect of anharmonicity. In the harmonic

approximation the distribution of distances has a gaussian shape and it is given by:

$$\rho(r) \cong \frac{1}{\sigma\sqrt{2\pi}} e^{-(r-R_c)^2/2\sigma^2} \tag{2.31}$$

An approximate expression of the first cumulants can be obtained through equation (2.29) which connects the local dynamics of the system i.e. to atomic relative displacements both parallel and perpendicular to the interatomic bond.

First cumulant C_1^*

The first EXAFS cumulant $C_1^* = \langle r \rangle$ is the average value of the instantaneous distance expressed by Eq. (2.29). In harmonic approximation $\langle \Delta u_{\parallel} \rangle$ and $\langle \Delta u_{\parallel} (\Delta u_{\perp})^2 \rangle$ are zero and one can see that [10,58]:

$$C_1^* = \langle r \rangle \cong R_c + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R_c} + \dots$$
 (2.32)

 R_c is the distance between the centers of thermal ellipsoids and coincides with the crystallographic distance. The last term in Eq. (2.32) depends on the Mean Square Relative Displacement, MSRD perpendicular to the bond direction. It is always positive, then the first cumulant C_1^* is larger than the crystallographic distance R_c and the difference grows with temperature. The term $\langle \Delta u_{\perp}^2 \rangle$ can be evaluated by inverting Eq. (2.32) if R_c is known from other techniques [36,38].

Second Cumulant C_2^*

The second EXAFS cumulant is the variance σ^2 of the distribution $\rho(r)$, i.e. MSRD of absorber and backscatter atoms:

$$C_2^* = \langle (r - \langle r \rangle)^2 \rangle \tag{2.33}$$

In harmonic approximation, substituting Eqs. (2.29) and (2.32) into (2.33) we obtained an approximate expression given by [59]:

$$C_2^* \cong \langle \Delta u_{\parallel}^2 \rangle - \frac{\langle \Delta u_{\parallel}^2 \Delta u_{\perp}^2 \rangle}{R_c^2} + \frac{[\langle \Delta u_{\perp}^4 \rangle - \langle \Delta u_{\perp}^2 \rangle]^2}{4R_c^2} + \dots$$
(2.34)

where the first term is the parallel MSRD and the third term is the variance of the distribution of $\langle \Delta u_{\perp}^2 \rangle$. It is customary to truncate equation (2.34) at the first order term [59]:

$$C_2^* \cong \langle \Delta u_{\parallel}^2 \rangle \tag{2.35}$$

The second EXAFS cumulant contains information about the thermal displacement parallel to the bond direction, taking into account the correlation of atomic motion.

Third cumulant C_3^*

The EXAFS third cumulant C_3^* measures the asymmetry of the distribution of distance $\rho(r)$ and depends on the 3^{rd} order force constant k_3 of the effective pair potential $V_{eff}(r)$ (see Eq. 2.30). It corresponds to the third central moment, $C_3^* = \langle (r - \langle r \rangle)^3 \rangle$ and according to the Eq. (2.29):

$$C_3^* = \langle \Delta u_{\parallel}^3 \rangle + (3/2R_c) [\langle \Delta u_{\parallel}^2 \Delta u_{\perp}^2 \rangle - \langle \Delta u_{\parallel}^2 \rangle \langle \Delta u_{\perp}^2 \rangle] + \dots$$
(2.36)

The lowest order term $\langle \Delta u_{\parallel}^3 \rangle$ in Eq. (2.36) corresponds to the parallel mean cubic relative displacement and in harmonic approximation it would be zero [60].

In the case of isotropy, $\langle \Delta u_{\perp}^2 \rangle = 2 \langle \Delta u_{\parallel}^2 \rangle = 2\sigma^2$. The second term in Eq. (2.36) is nonzero also for a harmonic crystal potential [60]; the third cumulant is then always different from zero, Therefore, the one dimensional distribution $\rho(r)$ is never gaussian [38].

However it has been demonstrated that the main contribution to the experimental third cumulant comes from the crystal anharmonicity, and the contribution of the vibrations perpendicular to the bond is negligible [10]. The knowledge of the third cumulant is important to obtain the useful information on the anharmonicity of the effective potential.



Figure 2.14. The interatomic distances between absorber and backscatter atom according to; Left: Diffraction, Right: EXAFS.

2.4 EXAFS versus Bragg diffraction

The difference between Bragg scattering and EXAFS is due to the different sensitivity of these two techniques to the correlation of atomic vibrations so that different information becomes available from the analysis of EXAFS spectra and Bragg diffraction patterns. A direct comparison between EXAFS and XRD measurements not only gives information about the correlation of atomic motion [61, 62] but also allows to obtain fundamental inputs to understand the connection between the bond length thermal expansion and macroscopic thermal expansion.

2.4.1 Interatomic distances

Let consider a pair of neighboring atoms (a) and (b) in a crystal and R_c be the distance between its equilibrium positions as shown in Fig. (2.14). Bragg diffraction is sensitive to the three- dimensional distributions of instantaneous positions r_a and r_b of the two atoms, and measures the distance between average positions, $R_c = |\langle r_b \rangle - \langle r_a \rangle|$ (Fig. 2.14, Right).

The temperature variation of the distance δR_c measures the macroscopic thermal expansion. EXAFS samples the one-dimensional distribution of distances and measures the average distance between instantaneous positions (see Fig. 2.14, Left), $\langle r \rangle = \langle |r_b - r_a| \rangle$. The distances R_c and $\langle r \rangle$ are in principle different: this difference of geometrical origin [58] is mainly due to the effect of relative vibrations perpendicular to the direction of the a - b bond. From a local perspective, recently R_c and $\langle r \rangle$ have been distinguished as "apparent" and "true" bond length, respectively [6].

Therefore, the thermal expansions measured by EXAFS and Bragg diffraction have a different physical meaning, they can be experimentally distinguished by accurate temperature dependent EXAFS and XRD measurements leading to the evaluation of the perpendicular mean square relative displacement (MSRD).

2.4.2 Thermal factors

Due to the different sensitivity of EXAFS and XRD to the correlation of atomic vibrations, Bragg diffraction thermal factors monitor the absolute movement of the atoms, while EXAFS is sensitive to the relative displacements. This difference allows one to evaluate the degree of correlation both parallel and perpendicular to the bond direction.

From Bragg diffraction refinement patterns one can get the displacement parameters U_{ij} of each atom, and the mean square displacements (MSD) can be calculated from these displacement parameters along selected directions. In our studies we are interested in the MSDs parallel and perpendicular to a given bond direction, U_{\parallel}^{i} and U_{\perp}^{i} , respectively, where i = a, b is a label for the absorber and backscatter atoms. EXAFS is sensitive to the relative displacements of atom b with respect to atom a ($\Delta u = u_b - u_a$).

Beni at al. [59] recognized long ago the sensitivity of EXAFS to the relative atomic motion along the bond direction: EXAFS Debye-waller factor directly gives information on the parallel mean square relative displacement $(MSRD_{\parallel})$ between absorber and back-scatter atoms. The possibility of obtaining from EXAFS the mean square relative displacement perpendicular to the interatomic bond $(MSRD_{\perp})$ was only recently exploited by Dalba et al. [36] and Fornasini et al [24].

Parallel MSRD $\langle u_{\parallel}^2 \rangle$

The parallel MSRD is directly measured by EXAFS as the variance of the distribution of interatomic distances, σ^2 [10,59] and given by the equation.

$$\langle \Delta u_{\parallel}^2 \rangle = \langle (R.u_a)^2 \rangle + \langle (R.u_b)^2 \rangle - 2 \langle (R.u_a)((R.u_b)) \rangle$$
(2.37)

In Eq. (2.37), the first two terms are corresponds to the uncorrelated MSDs measured by diffraction along the bond direction, $U^a_{\parallel} = \langle (R.u_a)^2 \rangle$ and $U^b_{\parallel} = \langle (R.u_b)^2 \rangle$, respectively and given by:

$$\langle \Delta u_{\parallel}^2 \rangle = \langle u_{b_{\parallel}}^2 \rangle + \langle u_{a_{\parallel}}^2 \rangle - 2 \langle u_{b_{\parallel}} u_{a_{\parallel}} \rangle \tag{2.38}$$

The third term in Eq. (2.38) is the parallel Displacement Correlation Function (DCF) [59], which depends on the correlation of atomic motion. The stronger correlation, the larger the DCF and the smaller C_2^* . The correlation term decreases with increasing the distance and vanishes after long distances.

Perpendicular MSRD $\langle u_{\perp}^2 \rangle$

The perpendicular MSRD $\langle \Delta u_{\perp}^2 \rangle$ is the projection of the total MSRD in a plane normal to the bond direction. It establishes the connection between the distances measured by EXAFS and by Bragg scattering. To a good approximation [57,58], $\langle u_{\perp}^2 \rangle$ is obtained from comparison of EXAFS and Crystallographic distances as in equation

$$\langle r \rangle = R_c + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R_c} \tag{2.39}$$

To the extent that $\langle \Delta u_{\perp}^2 \rangle$ increase with temperature, the thermal expansion measured by EXAFS is larger than the crystallographic thermal expansion measured by Bragg diffraction. Eq. (2.39) was known since long time [58], but only recently the difference between the nearest-neighbor distances measured by EXAFS and by diffraction has been experimentally detected in several systems, such as AgI [35], Ge [36], CuCl [38] and copper [24].

From the independent measurements of $\langle r \rangle$ and R_c , the perpendicular MSRD $\langle \Delta u_{\perp}^2 \rangle$ can be obtained by inversion of Eq. (2.39) [24,36]. Since $\langle \Delta u_{\perp}^2 \rangle$ is the projection of the relative displacement within a perpendicular plane, it should be divided by two before comparing with the MSDs $U_{\perp}^{a} + U_{\perp}^{b}$ measured by Bragg scattering [22], the residual difference being due to correlation in perpendicular direction as in Eq. (2.40):

$$\langle \Delta u_{\perp}^2 \rangle = \langle u_{b_{\perp}}^2 \rangle + \langle u_{a_{\perp}}^2 \rangle - 2 \langle u_{b_{\perp}} u_{a_{\perp}} \rangle \tag{2.40}$$

In some cases of high crystal symmetry, the thermal vibrations are isotropic around the equilibrium positions and the thermal ellipsoids reduce to spheres [63]. Therefore the parallel and perpendicular MSDs are given by [38, 56]:

$$\langle u_{i_{\parallel}}^2 \rangle = \frac{1}{3} \langle u_i^2 \rangle \tag{2.41}$$

$$\langle u_{i_{\perp}}^2 \rangle = \frac{2}{3} \langle u_i^2 \rangle \tag{2.42}$$

This difference is due to the different projections: the parallel MSD is projection along the bond direction while perpendicular MSD is on a plane normal to the bond [58]. Hence the $MSRD_{\perp}$ should be compared with twice the sum of the thermal factors of the atoms measured by diffraction.

The sensitivity to correlation is peculiar of EXAFS. As a consequence of long range averaging in diffraction experiments, the effect of short range correlations is dispersed into thermal diffuse scattering and the Debye-Waller factor measures only the uncorrelated MSD. Therefore, no complete information on correlation can be obtained from Bragg scattering.

One can show that the minimum and maximum possible values for parallel and perpendicular MSRDs can be calculated from the uncorrelated MSDs [22] corresponding to the relations:

$$\left(\sqrt{\langle u_{b_{\parallel}}^2 \rangle} - \sqrt{\langle u_{a_{\parallel}}^2 \rangle}\right)^2 \leq \langle \Delta u_{\parallel}^2 \rangle \leq \left(\sqrt{\langle u_{b_{\parallel}}^2 \rangle} + \sqrt{\langle u_{a_{\parallel}}^2 \rangle}\right)^2 \tag{2.43}$$

$$\left(\sqrt{\langle u_{b_{\perp}}^2 \rangle} - \sqrt{\langle u_{a_{\perp}}^2 \rangle}\right)^2 \leq \frac{\langle \Delta u_{\perp}^2 \rangle}{2} \leq \left(\sqrt{\langle u_{b_{\perp}}^2 \rangle} + \sqrt{\langle u_{a_{\perp}}^2 \rangle}\right)^2 \tag{2.44}$$

According to Eqs. (2.44, 2.44), the correlation between the vibrations of the two atoms in a certain direction can then be inferred. If the MSRD approaches the lower limit, the two atoms oscillate completely in phase or highly correlated in this direction and vice versa if the MSRD tends to the upper limit, the two atoms vibrate out of phase or anti-correlated.

2.4.3 Anisotropy of vibrations

In EXAFS, the relation between $\langle \Delta u_{\parallel}^2 \rangle$ and $\langle \Delta u_{\perp}^2 \rangle$ depends on the peculiar vibrational properties of the crystal. The ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle / \langle \Delta u_{\parallel}^2 \rangle$ measures the anisotropy of the relative vibration and it is 2 for the ideal isotropic relative vibrations crystal [64]. In the diffraction, the anisotropy γ is measured by the ratio U_{\perp}/U_{\parallel} for the MSDs.

Actually, relative atomic vibrations can never be a *priori* considered perfectly isotropic. As a consequence, the anisotropy γ is generally temperature dependent and its values can be much higher than two for some crystals. It is customary to refer to their asymptotic values for $T \rightarrow \infty$ [22, 36, 38].

The direct evaluation of these values can be difficult when the results are available only at low temperatures. At last, no a *priori* relations can be established between the shapes of absolute Bragg ellipsoids and that of relative EXAFS ellipsoids. The thermal factors of diffraction and that of EXAFS can have in addition, different anisotropy properties. EXAFS ellipsoids are generally anisotropic ($\gamma > 2$) also when Bragg ellipsoid are spherical: as a matter of fact in CuCl the MSDs are isotropic for symmetry reasons, while the MSRDs are significantly anisotropic [38].

The temperature dependence of the MSDs measured by diffraction can be described with reasonable accuracy by an Einstein model by:

$$U = \frac{\hbar}{2m\omega} \coth\left(\frac{\beta\hbar\omega}{2}\right) \tag{2.45}$$

where *m* is the atomic mass and $\omega = 2\pi\nu$ is the frequency of oscillation of each atom around its equilibrium position. The temperature dependence of the MSRDs measured by EXAFS can be described by correlated Einstein models, corresponding to Eq. (2.45), where 2m is substituted by 2μ for parallel MSRD and μ for perpendicular MSRD (μ is the reduced mass of absorber and backscatter atoms) [65].

For isotropic vibrations the frequencies are equal for parallel and perpendicular MSRDs and/or MSDs. Besides, the Einstein frequencies best-fitting the EXAFS MSRDs and diffraction MSDs are generally different. For the parallel and perpendicular MSRD, ω_{\parallel} and ω_{\perp} the frequencies of relative oscillation of absorber and backscatter atoms can be connected to effective bond-stretching and bond-bending force constants, respectively as given by:

$$\kappa_{\parallel} = \mu \omega_{\parallel}^2 \tag{2.46}$$

$$\kappa_{\perp} = \mu \omega_{\perp}^2 \tag{2.47}$$

The asymptotic value of the anisotropy γ can be obtained in more effective way from the ratio of the parallel and perpendicular force constants of the best-fitting Einstein models to the temperatures dependence of parallel and perpendicular MSRD as in equation:

$$\xi = \frac{\langle \Delta u_{\perp}^2 \rangle}{2 \langle \Delta u_{\parallel}^2 \rangle} = \frac{\kappa_{\parallel}}{\kappa_{\perp}} \tag{2.48}$$

For perfectly isotropy, $\xi = 1$.

2.5 Phenomenological models for EXAFS MSRDs

For parallel MSRD, the correlated Debye and Einstein models were developed quite early by Beni et al. [59] and Sevillano et al [66]. These models, specifically tailored to account for correlation, were obtained as phenomenological modifications of the familiar Debye and Einstein models used for specific heats and diffraction MSD. In addition to the original Debye model [16], the correlated Debye model assumes a further spherical approximation of the square moduli of eigenvectors [59,65,66] and applies only to cubic crystals with one atom per primitive cell (cubic Bravais crystals).

The Einstein model for specific heats approximates the phonon spectrum with a single frequency ω_E [16]. The correlated Einstein model [66] is generally cast into the different framework of the one-dimensional model of EXAFS, where it considers

the pair of absorber and backscatter atoms as an independent harmonic oscillator [61] with frequency ω_E . Anharmonic corrections and improvements to the original correlated Einstein model were successively proposed [67, 68].

The lattice dynamics of a crystal in harmonic approximation is described in terms of normal modes (q, λ) and general expressions of the parallel and perpendicular MSRDs in term of eigenfrequencies $\omega(q, \lambda)$ and eigenvectors $w_i(\lambda, q)$ of the dynamical matrix are given as [56, 60]:

$$MSRD_{\parallel} = \frac{1}{N} \sum_{q,\lambda} \langle |Q(q,\lambda,t)|^2 \rangle \left| \left(\frac{w_2(q,\lambda) \ e^{iq.R_c}}{\sqrt{M_2}} - \frac{w_1(q,\lambda)}{\sqrt{M_1}} \right) \cdot \hat{R}_c \right|^2$$
(2.49)

$$MSRD_{\perp} = \frac{1}{N} \sum_{q,\lambda} \langle |Q(q,\lambda,t)|^2 \rangle \times \left[\left\| \frac{w_2(\lambda,q) e^{(iq.R_c)}}{\sqrt{M_2}} - \frac{w_1(q,\lambda)}{\sqrt{M_1}} \right\|^2 - \left| \frac{w_2(\lambda,q) e^{(iq.R_c)}}{\sqrt{M_2}} - \frac{w_1(q,\lambda)}{\sqrt{M_1}} \cdot \hat{R}_c \right|^2 \right]$$
(2.50)

where M_1 and M_2 are the masses of the absorbing and backscattering atoms, respectively and N is the total number of unit cells. $w_k(q, \lambda)$ is the three-dimensional eigenvectors referred to the k atom in the primitive cell and gives the direction of atomic motion. $Q(q, \lambda, t)$ is the normal coordinate of mode (q, λ) , its average value depends on average energy $\langle E \rangle$ and frequency ω as:

$$\langle |Q(q,\lambda,t)|^2 \rangle = \frac{\langle E(q,\lambda) \rangle}{\omega^2(q,\lambda)} = \frac{\hbar}{2\omega(q,\lambda)} coth \frac{\hbar\omega(q,\lambda)}{2k_B T}$$
(2.51)

In the case of monatomic crystals with one atom per primitive cell, N is the total number of atoms and all the atoms have the same mass and same eigenvectors, the above equations becomes [59]:

$$MSRD_{\parallel} = \frac{1}{NM} \sum_{q,\lambda} \langle |Q(q,\lambda,t)|^2 \rangle \left| w(q,\lambda) \cdot \hat{R}_c \right|^2 \left| e^{iq.R_c} - 1 \right|^2$$
(2.52)

$$MSRD_{\perp} = \frac{1}{NM} \sum_{q,\lambda} \langle |Q(q,\lambda,t)|^2 \rangle \left[\left\| w(q,\lambda) \right\|^2 - \left| w(q,\lambda) \cdot \hat{R}_c \right|^2 \right] \left| e^{iq.R_c} - 1 \right|^2$$
(2.53)

2.5.1 Correlated-Einstein model

The Einstein model was developed to describe the temperature dependence of the heat capacity of the MSDs measured by diffraction, and considers each atom as an independent harmonic oscillator. In contrast, the correlated Einstein model is suited to account for the correlation effects on the MSRDs measured by EXAFS and assumes each pair of atom (absorber and backscatter atoms) to be an independent oscillator; the frequency of relative vibrations $\omega_E = \sqrt{k_0/\mu}$ depends on the force constant k_0 of the bond between the two atoms and on the reduced mass μ of atomic pair. Einstein model consists of approximating the phonon spectrum with a single Einstein frequency ω_E [16]:

$$\omega(\lambda, q) = \omega_E \qquad \lambda = 1, 2, ..., 3N \tag{2.54}$$

where N is the number of atoms in the unit cell and the maximum number of modes including acoustic and optic ones is 3N.

The Einstein model thus substitutes the phonon density of states $\rho(\omega)$ with delta function centered at ω_E and given by:

$$\rho^{ein}(\omega) = \delta(\omega - \omega_E) \tag{2.55}$$

According to this approximation and with Eqs. (2.49, 2.50), one can obtain the expression for the parallel and perpendicular MSRDs [56, 65, 69]:

$$MSRD_{\parallel}^{ein} = \frac{\hbar}{2\mu\omega_{\parallel}} \coth\left(\frac{\beta\hbar\omega_{\parallel}}{2}\right)$$
(2.56)

$$MSRD_{\perp}^{ein} = \frac{\hbar}{\mu\omega_{\perp}} \coth\left(\frac{\beta\hbar\omega_{\perp}}{2}\right)$$
(2.57)

The absolute values of $MSRD_{\parallel}(T)$ and $MSRD_{\perp}(T)$ can be obtained from the experimental temperature dependence of their relative values by fitting the following expressions [69] to experimental data:

$$\delta MSRD_{\parallel}(T) = \frac{\hbar}{2\mu\omega_{\parallel}} \coth\left(\frac{\beta\hbar\omega_{\perp}}{2}\right) - a_{\parallel}$$
(2.58)

$$\delta MSRD_{\perp}^{ein} = \frac{\hbar}{\mu\omega_{\perp}} \coth\left(\frac{\beta\hbar\omega_{\perp}}{2}\right) - a_{\perp}$$
(2.59)

where the zero-point values a_{\parallel} or a_{\perp} and the Einstein frequencies ω_{\parallel} or ω_{\perp} are the the only fitting parameters. Therefore the absolute values of the parallel and perpendicular MSRDs are obtained as [69]:

$$MSRD_{\parallel}(T) = \delta MSRD_{\parallel}(T) + a_{\parallel} \tag{2.60}$$

$$MSRD_{\perp}(T) = \delta MSRD_{\perp}(T) + a_{\perp} \tag{2.61}$$

The error deriving from this procedure should be taken into account to improve the accuracy of the MSRDs. Recently and for the first time the error owing to Einstein-fit model on absolute values of the EXAFS MSRDs has been estimated as a function of the standard deviation of the density of vibrational states [69]. In perfect Einstein crystal, where the DOS is a δ function and the DOS standard deviation is zero, the Einstein-fit error is zero.

One important application of this model is to recover the absolute values of the MSRD from the relative values of the MSRD determined through the analysis based on the ratio method. The success of the Einstein equation for the parallel MSRD has been related to its phenomenological interpretation which consider the absorber and backscatter atomic pair as an independent Einstein oscillator with frequency ω_E related to a local effective bond-stretching force constant $k = \mu \omega_E$ [61, 65] Einstein frequency has two meaning:

- an effective vibrational frequency of the interatomic bond
- a constant which roughly represents the centroid of the distribution of normal mode frequencies.

2.5.2 Correlated-Debye model

As a peculiar application of the original Debye model [16], the correlated Debye model considers the atomic pairs as harmonic oscillators with different frequency, and linearly approximates the phonon spectrum:

$$\omega(\lambda, q) = \nu_s q \qquad \lambda = 1, 2, 3 \tag{2.62}$$

where ν_s is the sound velocity in the crystal. A further spherical approximation is assumed for the eigenvectors [59, 66] in the CD model, and the first Brillouin zone is replaced by a sphere of radius q_D (Debye wave vector) containing the same number of wavevectors, N.

$$q_D = (6\pi^2 N/V)^{1/3} \tag{2.63}$$

where V is the total volume of the crystal. According to this approximations, CD model becomes best suitable for the acoustic branches and fails to model the optic branches which is independent of the phonon wave vector q [28]. The CD model applies only to cubic crystals with one atom per primitive cell (monatomic Bravis crystal) and characterized by a phonon (acoustic) density of state [56]:

$$\rho^{deb} \propto \omega^2 / \omega_D^3 \tag{2.64}$$

where ω_D is the characteristic Debye frequency and is related to the Debye temperature θ_D ; $\omega_D = \theta_D k_B/\hbar$, where k_B the Boltzman's constant and \hbar Planck's constant divided by 2π .

Then, according to these approximations and Eqs. (2.49, 2.50), the parallel and perpendicular MSRDs expression can be obtained [65, 66]:

$$MSRD_{\parallel}^{deb} = \frac{3\hbar}{M} \int_{0}^{\omega_{D}} d\omega \frac{\omega}{\omega_{D}^{3}} \coth(\beta\hbar\omega/2) \times \left[1 - \frac{\sin(\omega R_{c}/\nu_{s})}{(\omega R_{c}/\nu_{s})}\right]$$
(2.65)

$$MSRD_{\perp}^{deb} = \frac{6\hbar}{M} \int_{0}^{\omega_{D}} d\omega \frac{\omega}{\omega_{D}^{3}} \coth(\beta\hbar\omega/2) \times \left[1 - \frac{\sin(\omega R_{c}/\nu_{s})}{(\omega R_{c}/\nu_{s})}\right]$$
(2.66)

The situation for EXAFS is more complex than that for specific heats and diffraction; the general harmonic expressions of MSRDs Eqs. (2.49, 2.50), contains the correlation term and then the product of eigenvectors referred to different atoms within the primitive cell, for which a physically sound spherical average cannot be defined. Therefore the correlated Debye model for EXAFS MSRDs applies to the monatomic "Bravais" crystal and should not be extended to non-Bravais crystals [61].

The analytical expression for the perpendicular MSRD for Debye and/or Einstein model corresponds to the expression for the parallel MSRD apart from a factor 2 [65], this related to the fact that the perpendicular MSRD is a projection of relative atomic motion onto a plane, while the parallel MSRD is a projection along the bond direction. There is no a prior reason why for a given pair of atoms, the temperature dependence of parallel and perpendicular MSRDs should be best-fitted by the same Debye/Einstein frequency (or temperature).

2.6 EXAFS and Anharmonic potential

Anharmonic effective pair potential V_{eff} can be expressed as a function of the displacement as in Eq. (2.30), where third order force constant k_3 , is a measure of the asymmetry of distribution due to anharmonicity [14,67]: $V_{eff}(x) \simeq \frac{1}{2}\kappa_0 x^2 + \kappa_3 x^3 + \kappa_4 x^4 \dots$ It is well established that $V_{eff}(r)$ does not represent the true local interaction potential between absorber and backscatter atoms in the crystal. Then the introduction of an effective potential has been justified on the grounds that its shape seems to be insensitive to thermal changes [24]. Anyway, the position of the $V_{eff}(r)$ shifts with temperature and its asymmetry cannot reproduce the macroscopic thermal expansion [24].

In many atomic systems, the distribution of distances $\rho(r)$ has been related to a one-dimensional effective potential $V_{eff}(r)$ [59, 68, 70] and classically defined as in equation (2.26) and can be inverted to obtain V_{eff} :

$$V_{eff}(r) = (-1/\beta) \ln \rho(r) + const.$$
 (2.67)

In a quantum treatment the relation between $\rho(r)$ and V_{eff} is given by:

$$\rho(r) = Z^{-1} \langle r \mid e^{-\beta H_{eff}(r,p)} \mid r \rangle$$
(2.68)

where H_{eff} is the effective hamiltonian, connected to the effective potential by $H_{eff}(r, p) = p^2/(2\mu) + V_{eff}(r)$. Eq. (2.68) cannot be inverted as equation (2.26), therefore from EX-AFS experiment $V_{eff}(r)$ can be obtained only at sufficiently high temperatures when is safely in classical regime [71]. Anyway, the minimum of the potential corresponds to the maximum of the distribution in quantum regime. The connection between EXAFS cumulants and force constant of the interaction potential has been investigated for a two-atomic system leading to parameterized expressions of the cumulants as a function of the force constant of the one-dimensional *bare* interaction potential [67,72]. For many atomic systems, EXAFS cumulants can be connected by the same analytical expressions to the force constants of a one-dimensional effective pair potential.

The relationship between EXAFS cumulants and effective potential on one side and physical properties of many-atomic systems on the other, is still a matter of debate. In particular with reference to the very meaning of the effective potential [53,73] and its possible dependence on temperature [35,74]. The interest toward this subject has been enhanced by recent temperature dependent EXAFS studies, which have questioned the equivalence of the first and third cumulants for measuring the thermal expansion of interatomic bonds [24,36].

2.6.1 Classical approximation

The cumulants of effective distributions can be related in the classical approximation, to the lowest order force constants of the effective potential $V_{eff}(x)$ [29,75,76] which can be written in terms of the anharmonic pair potential parameters and the temperature [77] through the equations:

$$\delta C_1(T) = -\frac{3\kappa_3}{\kappa_0^2} k_B T - \dots \qquad (2.69)$$

$$C_2(T) = (\frac{k_B}{\kappa_0})T + \dots$$
 (2.70)

$$C_3(T) = -\frac{6\kappa_3}{\kappa_0^3} (k_B T)^2 - \dots$$
 (2.71)

$$C_4(T) = \frac{12}{\kappa_0^4} \left(\frac{9\kappa_3^2}{\kappa_0} - 2\kappa_4\right) (k_B T)^3 + \dots$$
 (2.72)

According to the first order of classical approximation, δC_1 and C_2 increase linearly with temperature but C_3 and C_4 are proportional to the square and cube of the temperature, respectively. The fitting to this behavior can be considered as a check of the
consistency of results obtained from EXAFS experiments.

By using theses expressions for the cumulants, the parameters of the anharmonic pair potential can be obtained through temperature dependent EXAFS data. Stern et al. [77] have obtained some expressions for several macroscopic characteristics of solids (the linear expansion coefficient, the Grüneisen parameter, Debye temperature, the bulk modulus) in terms of pair potential parameters.

2.6.2 Quantum treatments

Quantitive relations between EXAFS cumulants and force constants have been firstly proposed by Frenkel and Rehr [67] and extended by Yokoyama [72] using CE model and perturbation theory. EXAFS cumulants to the first order are given by [67]:

$$\delta C_1 = -\frac{3\kappa_3\sigma_0^2}{\kappa_0}\frac{1+z}{1-z} = -\frac{3\kappa_3}{\kappa_0}C_2$$
(2.73)

$$C_2 = \sigma_0^2 \frac{1+z}{1-z} = \frac{\hbar\omega}{2\kappa_0} \frac{1+z}{1-z}$$
(2.74)

$$C_3 = -\frac{2\kappa_3\sigma_0^4}{\kappa_0}\frac{z^2 + 10z + 1}{(1-z)^2} + \dots$$
(2.75)

$$C_4 = -\frac{12\kappa_4\sigma_0^8}{\hbar\omega}\frac{z^3 + 9z^2 + 9z + 1}{(1-z)^3} - \dots$$
(2.76)

where $z \equiv \exp^{-\beta\hbar\omega} = \exp^{-\theta_E/T}$ and $\theta_E = \hbar\omega/k_B$ is the Einstein temperature. $\sigma_0^2 = \hbar/2\mu\omega$ and $\omega = \sqrt{\kappa_0/\mu}$

According to these expressions, the behavior of the cumulants at high-temperature (HT) and low-temperature (LT) have been determined [67], they are shown in table (2.1). In the HT limit $(T \to \infty) \ z \cong 1 - (\hbar \omega / k_B T)$ but at LT limit $(T \to 0), \ z \to 0$ and we can neglect z^2 and the higher powers.

In table (2.1, HT), the formula at high temperature agree with the classical approach. These results are valid only to first order in κ_3 and simply to the first term in high-temperature series expansion [44, 67, 75].

At high temperature the classical approach can work well but cannot be valid at low temperature due to zero point vibration [78]. The low-temperature formula in table

Table 2.1. Approximate formulas for the cumulants at low-temperature (LT: $T \rightarrow 0$) and high-temperature (HT: $T \rightarrow \infty$) limits.

	LT $(T \rightarrow 0)$	HT $(T \to \infty)$
δC_1	- $\frac{3\kappa_3}{2\kappa_0^2}\hbar\omega(1+2z)$	- $\frac{3\kappa_3}{\kappa_0^2}k_BT$
C_2	$\frac{\hbar\omega}{2\kappa_0}(1+2z)$	$\frac{1}{\kappa_0}k_BT$
C_3	- $\frac{\kappa_3}{2\kappa_0^3} (\hbar\omega)^2 (1+12z)$	- $\frac{6\kappa_3}{\kappa_0^3}(k_BT)^2$

(2.1, LT), can account for the zero point contributions which derived with the quantum treatment. Hung et al. [68] has been developed quantum treatment by considering anharmonic CE model to account for anharmonicity of the EXAFS cumulants.

The correlated Einstein model is local and should be a reasonable approximation when correlations are short range. The above relations derived by Frenkel and Rehr [67] of EXAFS cumulants using correlated Einestein model and first order thermodynamics perturbation theory and their discussion is based on a local vibration picture and includes near-neighbor correlations.

2.6.3 Thermal expansion

The true bond thermal expansion is measured by the temperature variation of the EXAFS first cumulant. For a two atomic system, the thermal expansion measured by the first cumulant is solely due to the asymmetry of the interaction potential and is often considered equivalent to the joint knowledge of the second and third cumulant.

This is however highly questionable for many atomic systems, where it amounts to attributing thermal expansion solely to the asymmetry of the effective pair potential and can be independently obtained by the quantity $a = -3(\kappa_3/\kappa_0)C_2^*$, where κ_0 and κ_3 are the second and third order force constants, respectively [67]. κ_0 and κ_3 can be

obtained by fitting suitable models to the temperature dependence of the second and third EXAFS cumulant. One of the theoretical models according to the perturbative quantum approach of Refs. [67, 72] can be used to fitting the temperature dependence of the third cumulant.

There is no a *prior* relationship between thermal expansion and third cumulant, so that in general the quantity a cannot be considered as a measure of thermal expansion. The connection between the crystal potential and one-dimensional EXAFS distribution of distances and its effective potential is far from trivial. The EXAFS effective potential for a crystal is in principle temperature dependent, both in position and shape. It was experimentally established that the thermal expansion due to the asymmetry of the potential corresponding to the quantity "a" does not correspond to (is much weaker) the true bond expansion measured by the first EXAFS cumulant for Copper [24], Ge [36] and CuCl [38].

Chapter 3

NTE in Tetrahedrally bonded crystals

3.1 Introduction

The crystals of zincblende structure consist of two interpenetrating fcc lattices of different atoms, each atom is tetrahedrally coordinated to four atoms of the other species as shown in Fig. (3.1). The diamond structure can be consider as a particular case of zincblende where all atoms are equal. The materials of open structure with low coordination number, including many important semiconductors have attracted much experimental and theoretical attention. Their vibrational and associated thermal properties show interesting features, including a low frequency transverse acoustic branch which is important at low temperatures and leads in many cases to negative values of the expansion coefficient.

For a material at a given temperature, many different vibration modes are excited but not all contribute to NTE. At low temperature, the low frequency transverse vibrational modes are preferentially excited and they have negative values of Grüneisen parameter γ_i , then several materials exhibit NTE when such modes predominate. The importance of low-energy transverse acoustic (TA) modes at Brillouin zone-boundary was early recognized from the pressure dependence of phonon frequencies [79]. Blackman (1957) was the first one who pointed out that the open structure crystals would



Figure 3.1. The conventional fcc unit cell of zincblende crystals.

favor "guitar-string"- like TA modes which soften under pressure and could lead to NTE if such modes are sufficiently weighted [80].

Another simple picture has been given by Barron (1957): due to thermal vibrations an atom becomes displaced from its equilibrium position, it exerts an attractive force on those neighboring atoms which are in directions perpendicular to the displacement, thus tending to contract the crystal [81].

Lattice dynamical properties were successively calculated through empirical models [82] and *ab* initio density functional theories [83,84]. The interest in studying the Negative Thermal expansion in diamond crystals (Si and Ge) dates back since the early 1960s [85–87]. Theoretical calculations have reproduced low temperature expansion coefficient of Si and shown that the TA (X) and TA (L) modes have polarizations associated with pure bending motion, the bonds between atoms are either undisturbed or distorted only by atomic motion perpendicular to the bonds [32].

In zincblende structure, the recent *ab* initio calculations [88] on CuCl show that the frequency of the transverse acoustic (TA) mode at zone boundary points (X and L) decreases with decreasing volume or increasing pressure, thus indicating a negative Grüneisen parameter for these modes and consequently contributing to NTE.



Figure 3.2. Calculated phonon-dispersion curves along the high symmetry directions and phonon density of state (DOS) for CdTe compared with the experimental inelastic neutron-scattering data (Circles), the figure is taken from Ref. [93]

The structural, elastic and thermodynamic properties of CdTe have been investigated by molecular-dynamics (MD) simulation [89]. Recently, ab initio calculations have been performed to investigate elastic, electronic and lattice dynamics properties of CdTe [90]. The calculated lattice parameters, elastic constants and phonon dispersions are in good agreement with available experimental and theoretical results [90]. The phonon density of states and specific heats of CdTe were calculated used the adiabatic bond-charge model [91] and compared with both the experimental data [92] and the results of other models which give a good description of its lattice dynamics. The phonon dispersion relation of CdTe has been calculated [93] along high symmetry directions of the first Brillouin zone (see Fig. 3.2): $\Gamma \to X \equiv [\xi, 0, 0], K \to \Gamma \equiv [\xi, \xi, 0]$ and $\Gamma \to L \equiv [\xi, \xi, \xi]$. The calculated data are in excellent agreement with the experimental data measured using neutron inelastic scattering [92] as shown in Fig. (3.2).

3.2 Elastic properties of Zincblende structure

The elastic constants give important information concerning the nature of the forces operating in the solids, in particular they provide information on the stability and stiffness of materials. There are different ways of treating elasticity and of defining elastic coefficients. For treating elasticity and defining the elastic constant we will be concerned with the "stress-strain" coefficients. Elastic behavior is described in terms of stress (force per unit area) and strain (relative change of dimensions) and defined either by compliance (response of a material to applied stress), or its reciprocal stiffness (the bulk modulus) which describes its resistance to applied strain. The bulk modulus $B_T = -V(\partial P/\partial V)_T$ describes the resistance to volume change under a hydrostatic pressure. The generalization of this concept leads to the definition of the linear elastic constant tensor (stiffnesses), defined by:

$$c_{\alpha\beta,\gamma\delta}^{T} = \left(\frac{\partial\sigma_{\alpha\beta}}{\partial\eta_{\gamma\delta}}\right)_{\eta,T} \tag{3.1}$$

where $\sigma_{\alpha\beta}$ denotes the Cauchy stress tensor and $\eta_{\gamma\delta}$ is the Lagrange finite-strain tensor. The subscript $\dot{\eta}$ means that all other strain coordinates are kept constant. Then, the stiffness describes how each stress coordinate changes when only one strain coordinate is changed. Normally the stress and strain tensors are symmetric, $\sigma_{\alpha\beta} = \sigma_{\beta\alpha} = \sigma_{\lambda}$ and $\eta_{\gamma\delta} = \eta_{\delta\gamma} = \eta_{\mu}$ and have only six independent elements. The positive and negative diagonal elements of $\sigma_{\alpha\beta}$ indicate a tension or a compression along the given direction, respectively. Off-diagonal elements and also differences between the diagonal elements indicates shear stress. For a solid under hydrostatic pressure "P", all the off-diagonal elements vanish and $\sigma_{\alpha\beta} = -P\delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is equal to unity when $\alpha = \beta$ and zero when they are different.

The number of independent coefficients of the elastic tensor depends upon symmetry. If the stress is isotropic, $c_{\lambda,\mu} = c_{\mu,\lambda}$, reducing the number of independent coefficients to 21. The crystal symmetry further reduces this number, the cubic crystals have only three elastic constants: $c_{11} = c_{xx,xx}$, $c_{12} = c_{xx,yy}$, $c_{44} = c_{yz,yz}$. In isotropic materials where all directions are equivalent the elastic constants, $c_{11} = c_{22} = c_{33}$, etc, $c_{44} = (c_{11} - c_{12})/2$ and other stiffnesses, such as c_{14} , c_{15} and c_{45} are zero. The experimental elastic constants of zincblende material have been obtained at room temperature [94] and table (3.8) shows the elastic constants of Ge, CdTe and CuCl.

Crystal	$r(\text{\AA})$	C_0	c_{11}	c_{12}	c_{44}	B_s	C_s .
Ge	4.63	6.4	12.89	4.83	6.71	7.5	4
CdTe	5.30	3.72	5.35	3.68	1.99	4.2	0.8
CuCl	4.42	7.68	2.72	1.87	1.57	2.2	0.4

Table 3.1. Experimental bond length, elastic constants $(10^{10}N/m^2)$, bulk and shear moduli for Ge, CdTe and CuCl crystals [94].

For cubic crystals, the knowledge of elastic constants c_{11}, c_{12} and c_{44} makes it possible to determine the bulk and shear modulus. The bulk modulus (B_s) and the shear modulus (C_s) both are true stiffnesses and are given respectively by the relations:

$$B_s = \frac{(c_{11} + 2c_{12})}{3} \tag{3.2}$$

$$C_s = \frac{(c_{11} - c_{12})}{2} \tag{3.3}$$

The elastic properties of a material are basically determined by the interactions of electrons. Dimensional analysis thus suggests that the elastic constants should be of the order of magnitude " e^2/r^4 ", where "e" is the electronic charge and "r" is the distance between nearest neighbor atoms [94]. This principle has been applied to the zincblende crystals by defining an elastic constant $C_0 \equiv e^2/r^4$. Then an instructive comparison and the regularities of the elastic properties on more quantitative basis are developed by considering the reduced elastic constants which are defined as, $c_{11}^* = c_{11}/C_0$, etc., where C_0 is the normalization modulus. Thus the reduced bulk and shear moduli are $B^* = B_s/C_0$ and $C_s^* = C_s/C_0$, respectively.

This choice of the normalization to the elastic properties of the crystals is suggested by the fact that all forces in the crystal are basically electrostatic in origin. considering all crystals have the same symmetry, the same number of valence electrons per atom pair and thus similar bonding; then the dependence of the elastic moduli on the bond length is largely removed. Therefore, the regularities in the reduced elastic moduli



Figure 3.3. The reduced Bulk modulus and shear moduli of the tetrahedra semiconductors as a function of the bond ionicity f_i , the figure is taken from Ref. [94].

should be directly correlated with the character of the bond (see Fig. 3.3). In table 3.8 shows that the reduced bulk and shear moduli B^* and C_s^* are decreases as the ionicity increases from Ge to CuCl but do not show a systematic variation.

Fig. (3.3), shows the reduced bulk and shear moduli as a function of the bond ionicity and reflect strong variation between the different rows of the Periodic table. The semiconductor compounds formed from elements of the group III and V of the periodic table (such as GaAs) have properties very similar to the group IV elements (e.g. Ge). Going from the group IV elements to the III-V compounds, the bonding becomes partly ionic. The ionicity increases the Coulomb interaction between the ions and also the energy of the fundamental gap in the electronic band structure, then it causes significant changes in the semiconductor properties. The ionicity becomes more even larger and more important in the II-VI compounds such as CdTe which have band gaps larger than 1 eV but the I-VII compounds (e.g. CuCl) tend to have even larger band gaps (> 3eV) as a result of their higher ionicity [95].

The regularities in the elastic properties of the diamond and zincblende crystals have been explained in terms of the bond ionicity, f_i . The scale of the bond ionicity



Figure 3.4. The calculated pressure-dependence of elastic constants and bulk modulus for CdTe, the figure is taken from Ref. [90].

is defined by Phillips and Van Vechten for heteropolar crystals and demonstrates that the ionicity correlates well with the crystal structure and only crystals with f_i less than a critical value are stable in tetrahedrally coordinate structure [30, 31]. The reduced shear moduli in Fig. (3.3) is decrease as the bond ionicity increases, so that their values should decrease and tend to zero in the ionic limit $f_i \rightarrow 1$. CuCl is the only compound found in the ZB structure have ionicity very near to the critical value and show a great disagreement with the trend in Fig. (3.3).

At low temperature, the low energy transverse acoustic modes are excited and supported by the low shear moduli of the materials, i.e. less rigidity. Recently, the pressure dependence of the elastic constants of CdTe has been determined up to 3 GPa. It was found that both c_{11} and c_{12} increase monotonically with pressure whereas the slope for c_{44} is slightly smaller as shown in Fig. (3.4).



Figure 3.5. schematic representation of the bond length and angles between neighboring atoms of cubic ZB structure considered to belong to the unit cell containing atoms 1 and 2 and atypical angle θ_{14}^1 .

3.2.1 Valence-Force Field model (VFF)

In open structure crystals, short range (non-central) forces extend to further neighbors and play an important role in their stabilization. The most useful phenomenological description of the short-range forces in tetrahedrally coordinated crystals is the Valence force field (VFF) approach [96]. By resolving all interatomic forces into bondstretching (α) and bond-bending (β) forces, the VFF approach takes into account the interactions between neighboring bond lengths and bond angles as shown in Fig. (3.5). There are two primary advantages of the VFF model; (i) the model is automatically rotationally invariant and all the distortion energies are described in terms of bond lengths and angles. (ii) In crystals where atom pair bonds play a major role, the VFF is the most natural description of interatomic forces.

The VFF model for diamond-structure crystals, simplified by omitting the less im-

portant forces and the distortion energy of each unit cell, is given by [94]:

$$U = \frac{1}{2} \sum_{i=1}^{4} k_r (\Delta r_i)^2 + \sum_{s=1}^{2} \left[\frac{1}{2} \sum_{i,j>i} k_{\theta}^s (r \Delta \theta_{ij}^s)^2 + \sum_{i,j\neq i} k_{r\theta} (\Delta r_i^s) (r \Delta \theta_{ij}^s) + \sum_{i,j>i} k_{rr}^s (\Delta r_i^s) (\Delta r_j^s) \right]$$
(3.4)

where k_r and k_{θ} are the bond length and angles, respectively. The force constants k_{θ}^s , etc. are different for two atoms in the unit cell (s=1, 2). The bonds about each atom are denoted by i, j = 1, ..., 4, r is the equilibrium bond length, Δr_i^s is the scalar change in length of bond i about atom s and $\Delta \theta_{ij}^s$ is the change in angle formed by bonds i and jabout s as shown in Fig. (3.5). Taking in this case the force constants for two atoms in the unit cell always enter the relevant quantities in the form $k = k^1 + k^2$ and deal with a smaller set of independent constants, $k_r, k_{\theta} = \frac{1}{2}(k_{\theta}^1 + k_{\theta}^2)$, etc.. Assuming the rigid point ions with charges $\pm Z^*$ for Coulomb energy which interact via coulomb potential $\pm Z^* e^2/\epsilon R$ where R is the separation and ϵ is the electronic dielectric constant. for the stability of the crystal, it must also include the effect of the linear repulsive term in addition to the purely Coulomb forces, then there must be a linear bond-stretching term in addition to Eq. (3.4):

$$U = \sum_{i=1}^{4} f_r \Delta r_i + second - order terms$$
(3.5)

where $f_r = -\frac{1}{4} \alpha_M Z^{*2} e^2 / \epsilon r^2$ the condition that the crystal be in equilibrium and also proportional to Z^{*2}/ϵ , then it is conveniently included with the Coulomb terms. The contribution of the coulomb forces to the elastic constants has been given by Blackman [27]. Therefore, the expressions for the elastic constants have been derived by directly expanding Eq. (3.4) and using Blackman and Eq. (3.5), the results are depending on k_r, k_{θ} , etc. [94].

The formulas for the elastic constants can be further simplified through an approximation suggested by Keating [97]. The expansion of the VFF energy U in Eq. (3.6) is written as a function of scalar variations products of bond vectors $\Delta(r_i^s.r_j^s)$, where r_i^s and r_j^s are bond vectors about atom s and is given by:

$$U = \frac{1}{2}\alpha \left(\frac{3}{4r^2}\right) \sum_{i=1}^{4} [\Delta(r_i^1 \cdot r_i^1)]^2 + \frac{1}{2} \sum_{s=1}^{2} \beta^s \left(\frac{3}{4r^2}\right) \sum_{i,j>i} [\Delta(r_i^s \cdot r_j^s)]^2$$
(3.6)

where " α " and " β " are bond-stretching and bond-bending force constants, respectively and different for the two atoms (s=1, 2) in the primitive unit cell. In terms of changes in bond length and angles, Keating's approximation is connected to the VFF by considering:

$$k_r = 3\alpha + \beta/2, \ k_\theta = 2\beta/3, \ k_{rr} = \frac{1}{12}\beta, \ k_{r\dot{\theta}} = (3\sqrt{2})^{-1}\beta.$$
 (3.7)

Then the elastic constants according to Keating's approximation of the VFF model in tetrahedral structure are defined as [94]:

$$c_{11} + 2c_{12} = (\sqrt{3}/4r)(3\alpha + \beta) - 0.355SC_0$$
(3.8)

$$c_{11} - c_{12} = (\sqrt{3}/r)\beta + 0.053SC_0 \tag{3.9}$$

$$c_{44} = (\sqrt{3}/4r)(\alpha + \beta) - 0.136SC_0 - C\zeta^2$$
(3.10)

where C_0 is the normalization modulus, S the effective charge parameter and ζ is the internal strain parameter defined by Kleinman and given by [98]:

$$\zeta = C^{-1}[(\sqrt{3}/4r)(\alpha - \beta) - 0.294SC_0, \qquad (3.11)$$

$$C = (\sqrt{3}/4r)(\alpha - \beta) - 0.266SC_0 \tag{3.12}$$

From the experimental data of the elastic constants of the diamond and zincblende crystals, the short range force parameters for Keating's approximation α and β can be derived [94]. Table 3.2 shows the calculated short range force parameters α and β from the obtained elastic constants of the ZB crystals. In table (3.2), the calculated values of α and β decrease with increasing the bond ionicity. From Eq. (3.8), the reduced shear moduli should decrease as the ionicity increases because they are primarily determined by β , whose value should decrease and tend to zero in the ionic limit $f_i \rightarrow 1$ as shown in Fig. (3.3).

The behavior of the elastic constants is best understood by examining the derived parameters of the "central" force α and "non-central" force β as a function of f_i . Fig. (3.6) shows the values of β/α as a function of the bond ionicity and represents the ratio of the noncentral to the central force constants, $\beta/\alpha = 0$ for $f_i \rightarrow 1$. Then the primary trends in the elastic constants are described quantitatively by [28]:

$$\beta/\alpha = 0.3(1 - f_i) \tag{3.13}$$

Table 3.2. The calculated values of the bond-stretching (α) and bond-bending (β) forces parameters for Keating's approximation of the VFF model and phillips ionicity (f_i), the values are taken from Ref. [94].

Crystal	$\alpha~[{\rm N/m}]$	$\beta~[{\rm N/m}]$	$\beta/lpha$	f_i
Ge	38.67	11.35	0.294	0
CdTe	29.02	2.43	0.084	0.675
CuCl	12.60	1.00	0.079	0.746



Figure 3.6. The ratio of non-central to central force constants β/α as a function of the bond ionicity f_i , the figure is taken from Ref. [28]

This is the simplest possible form having the required result $\beta = 0$ for $f_i = 1$. This result provides a simple picture of the experimental force constants as a function of the bond ionicity and tetrahedrally bonded structure are then expected to have weak noncentral forces β . The dimensionless ratio β/α measures the importance of the covalent bond in determining the stability of the tetrahedral structure: its value decreases with increasing the bond ionicity [30].

3.3 NTE in zincblende structure

A simple phenomenological interpretation of NTE in zincblende and diamond structures was formulated since long ago by considering the $[1\bar{1}0]$ polarizations of the [110] transverse acoustic modes [99]. These modes correspond to planes of atoms moving as a unit perpendicular to the direction of all nearest neighbor bonds which are not in the plane. Fig. (3.7), shows a schematic illustration of how the transverse vibrations can propagate along chains with a quite open space normal to the bond direction of propagation from three-dimensional model of the structure. Unless the bonds have strong angular rigidity, this vibrations will have relatively low frequency and could soften under pressure, that is decrease in frequency like a relaxed guitar string [3,100]. Therefore, these low frequency TA modes are the most likely to have negative Grüneisen parameters, leading to NTE if such modes are sufficiently weighted. This conclusion was supported also by old central force models [27].

The measurements of ultrasonic wave velocity for the [110] TA modes with [110] polarizations and corresponding to the shear elastic modulus $(C_s = \frac{1}{2}(c_{11} - c_{12}))$ of the diamond and zincblende crystals, show that the pressure derivative dv_i/dP of the velocity is negative for many of these crystals in a limited temperature interval. The most negative compound being the CuCl, where the bonds are most ionic and therefore less rigid. The weighting of this soft mode at low temperatures leads to the negative expansion and then to the crystal contraction as in Si, Ge, CdTe and CuCl.

The negative expansion is more marked and extends to higher temperatures for



Figure 3.7. schematic illustration of the "chains" of atoms in the [110] direction in the cubic lattice along which the lowest-frequency TA acoustic waves are propagated.

crystals in which the charge separation is large and there is more ionic character. According to the Phillips ionicity factor [30], CuCl is the most ionic tetrahedrally bonded system and has the largest NTE coefficient ($\alpha_{min} \sim -9 \times 10^{-6} K^{-1}$) [18] and NTE extended up to 100K as shown in Fig. (3.8). Conversely in the diamond structure there is no charge separation and covalent bonding is very strong and expansion is positive nearly at all temperatures, Ge [36] has negative expansion extending from 15K to 40K and has very weak NTE $\alpha_{min} \sim -0.07 \times 10^{-6} K^{-1}$.

Diamond and zincblende structures have NTE only in a restricted temperature interval but at high temperatures show positive expansion. For many of them the thermal expansion coefficient is small because of their low limiting Grüneisen function $\gamma(T \to \infty)$ (see Fig. 1.4) and low compressibility. It is worth noting that, NTE is not observed in crystals were the ionicity is larger than in CuCl, inducing the change from zincblende structure to the rock salt structure [30].

In zincblende structure, the values of Grüneisen parameter, γ_j is positive at high temperatures as contrasted with negative value at very low temperatures (see Fig. 1.4). In the weighting of the γ_j , if the relatively highly weighted vibrations have a negative



Figure 3.8. Thermal expansion coefficient for selected tetrahedrally bonded crystals.

contribution to form the average value of Grüneisen function γ ; then an overall contribution can be negative and give rise to negative expansion.

In conclusion, in tetrahedrally bonded cubic semiconductors, the NTE is isotropic and limited to a low-temperature interval, its extent increases with the bond ionicity from Ge were it is weak to CuCl the strongest (Fig. 3.8) [18]. In the compounds, the negative contribution to thermal expansion is overcome by the positive contribution when temperature increases and has been attributed to low-frequency transverse acoustic modes with negative Grüneisen parameter whose effect is dominant in a limited temperature interval.

3.4 EXAFS studies of NTE zincblende crystals

EXAFS is a powerful probe for studying the local behavior of NTE materials. Bragg diffraction can give only partial information on the local behavior and EXAFS is particularly suited for complementing this information. EXAFS is sensitive to correlation of atomic vibrations and can give unique insights on the local thermal behavior of materials. The same sensitivity to correlation and similar information can in principle be obtained from the analysis of the diffuse scattering. The main strength and limitation of EXAFS are the selectivity of atomic species and insensitivity to long-range order, respectively.

In the last years, the possibility of obtaining complementary information on local structure and dynamics on the diamond and zincblende crystals from EXAFS has been experimentally demonstrated. New perspectives for getting deeper insights on local origin of NTE have been recently opened by the progresses in EXAFS analysis and interpretation related to the possibility of accurately measuring:

- the thermal expansion of the nearest-neighbors bond distance (true-bond expansion)
- the perpendicular mean square relative displacement (MSRD)

The relative perpendicular vibrations measured by EXAFS are related to the tension mechanism and to the transverse acoustic modes which are considered responsible for NTE in Zincblende structure. EXAFS results are consistent with phenomenological models of NTE based on the competition between stretching and tension effects. The ratio of perpendicular to parallel MSRDs measures the anisotropy of relative atomic vibrations which can be connected to NTE.

It is convenient to focus the attention on crystals of relatively simple structure such as diamond-zincblende tetrahedrally bonded crystals, to evaluate the strength and limitations of EXAFS for quantitive studies of NTE. The NTE in the diamond and zincblende crystals is observed at low temperature and NTE is quite weak in Ge and strongest in CuCl (see Fig. 3.8). Recent EXAFS studies on Ge [36] and CuCl [38] have shown that in both crystals:

(i) The nearest neighbor bond expansion is always positive, the stronger is the NTE measured by Bragg diffraction, the larger is the positive thermal expansion (PTE)

measured by EXAFS. This differences between bond PTE and lattice NTE is due to the effect of perpendicular vibration.

(ii) The relative atomic vibrations measured by EXAFS are anisotropic. Anisotropy of Ge and CuCl is temperature dependent, its asymptotic values are 6 and 11, respectively. CuCl has larger anisotropy related to the the presence of intense motion perpendicular to a given bond and connected to the tension effect that give rise to the stronger NTE. Therefore, the tension effect giving rise to NTE can be correlated to the anisotropy of the mean square relative displacements.

The obtained results for Ge and CuCl suggested the existence of a correlation between the NTE properties and anisotropy of relative vibrations measured by EXAFS. To confirm this correlation and search for its quantitative assessment, EXAFS measurements on CdTe whose NTE properties are intermediate between those of Ge and CuCl, have been performed. In this work, we will present the analysis of EXAFS spectra of CdTe and compare the results with the obtained results on the other zincblende crystals, Ge and CuCl.

Chapter 4

EXAFS OF CdTe

4.1 EXAFS Experiment and data reduction

EXAFS measurements have been done at the beamline BM29 of ESRF (European Synchrotron Radiation Facility) in Grenoble, France [101] at the Cd K-edge in CdTe.

4.1.1 Sample preparation

The structural purity of the sample had been checked before performing EXAFS measurements. Cadmium Telluride powders, 99.999 % pure (from Alfa Aesar) had been structurally tested by X-ray diffraction using an X'Pert PRO diffractometer at the physics department of Trento, with CuK_{α} target at room temperature, see Fig. (4.1).

A homogeneous sample was prepared by dispersing the CdTe powder in methyl alcohol within an ultrasonic mixer and letting the suspension to precipitate slowly on polytetrafluoroethylene membranes (see Fig. 4.2). To optimize the signal to noise ratio of the EXAFS signal, about 50 mg/cm² of CdTe were deposited to have an edge jump, $\mu x \simeq 1$ at Cd K-edge, where μ is the linear absorption coefficient and x is the sample thickness. The sample was loaded and carefully fixed in a sample holder, the holder was inserted in the evacuated measurement chamber. The sample holder was attached to an arm connected to a step motor to control the vertical position of the sample, while its horizontal position was controlled by moving of the chamber itself in front of the beam.



Figure 4.1. Powder X-ray diffraction spectrum of CdTe (space group F3m) at room temperature and Cu K_{α} as a target.



Figure 4.2. The setup for preparing homogeneous films of CdTe from the suspensions of the fine powder in methyl alcohol.

4.1.2 EXAFS Measurements

The beamline BM29 is the general purpose X-ray absorption spectroscopy (XAS) beam line at the ESRF [101]. It originates from bending magnet and can cover a very large operational energy range, from 4 keV to 74 keV; the energy resolution is typically a factor of 3 to 5 better than the intrinsic spectral broadening at any K or L absorption edge. A signal to noise ratio above 7.0×10^4 can be achieved for well prepared samples and high beam stability.

The monochromator is a double silicon crystal of fixed exit type, different reflecting faces are available, Si(111), Si(220), Si(311) and Si(511), depending on the requirements for x-ray flux and energy. Frequently the monochromator is accompanied by one or more X-ray mirrors, these mirrors are based on the phenomenon of total reflection and their aims are to reject the harmonics and to collimate and focalized the beam.

EXAFS measurements on CdTe have been performed with synchrotron radiation in transmission mode in the beamline BM29 [101] as shown in Fig. (4.3). The electron energy and the average current of the storage ring were 6 GeV and 190 mA, respectively.

The X-ray beam was monochromatized by two parallel silicon crystals with flat (311)



Figure 4.3. Schematic representation of a typical X-ray absorption experiment in a transmission mode

reflecting faces. Harmonic influence was reduced by the reflection from two Pt-coated mirrors. The energy of the incident x-rays was scanned in the range 26400 - 28230 eV, with ΔE step varying from 0.5 eV in the near-edge region (Cd K-edge at 26711 eV) to 5 eV at the end of the spectra, in order to obtain a uniform $\Delta k = 0.025$ Å step in the EXAFS region.

The size of the beam incident on the sample was about $4 \times 2 \text{ mm}^2$. The incoming and outgoing photon fluxes were measured by two ionization chambers filled with krypton gas; at pressures of 140 and 500 mbar, respectively.

The temperature dependent EXAFS measurements on CdTe were done from 19 K to 300 K. The sample temperature was varied at steps from 25 K at low temperature (below 150 K) to 50 K up to room temperature. To thermalize the sample, a liquid helium cryostat was utilized where the sample itself was immersed in "He" gas atmosphere. The temperature control was achieved through an electric heater controlled by a feedback loop. The thermal stabilization was guaranteed within 1 K, where two or three spectra were collected at each temperature to allow an evaluation of the experimental uncertainty.

4.1.3 EXAFS data reduction procedure

The output results of measurements are the incident and transmitted X-ray beam intensities I_0 and I, respectively. The X-ray absorption coefficient $\mu x = \ln (I_0/I)$ is shown in Fig. (4.4, continuous line).

4.1.4 Extraction of EXAFS signal

The extraction of the EXAFS signals $\chi(k)$ from the experimental spectra $x\mu(E)$ of the CdTe at different temperature was performed according to well established procedure [38, 71] using the EXTRA code [102]. A strait line best fitting the pre-edge signal in the energy range from 26450 to 26550 eV (see Fig. 4.4, dashed line) was preliminarily subtracted from the whole EXAFS spectra. This region is essentially a global background for the XAFS spectrum of the K-edge of cadmium.

After the "pre-edge removal", the edges of all experimental spectra have been aligned to have the same energy grid, in order to obtain reliable values of the interatomic distances. The alignment procedure was done by best-fitting the edge region of all EXAFS spectra at different temperatures to the edge region of reference spectrum, at 19K within 0.1 eV, in order to obtain a resolution better than 0.001 Å in distance variations.



Figure 4.4. X-ray absorption spectrum at Cd K-edge of CdTe measured at 19K (line) and pre-edg linear fit(dashed line). In the inset the absorption coefficient (continuous line) is plotted with the smooth background μ_0 (dotted line)as a function of the photoelectron wave vector k.

The second step is to convert the coordinates from the energy space E to the wave number space k as shown in Eq. (4.1). The evaluation of core electron binding energy E_b is very important, its uncertainty introduces a phase shift of the EXAFS signal and consequently an error on the analysis of interatomic distance. Here k has been experimentally determined as

$$k = \sqrt{\frac{2m}{\hbar^2} \left(\hbar\omega - E_s\right)} \tag{4.1}$$

where $k = 0.51233\sqrt{(\hbar\omega - E_s)}$ for a wave number measured in Å⁻¹ and energies in eV. The values of k have been calculated with respect to an energy origin E_s set at the maximum of the first derivative of a spectrum chosen as a reference ($E_s = 26719.82$ at 19K as a reference). The edges of all other spectra have been aligned to within 0.1 eV

with respect to the reference, in order to guarantee a resolution better than 0.001 Å in the evaluation of relative distances.

To evaluate μ_0 we search for a curve that can average the oscillations present on the X-ray absorption coefficient by a polynomial function; an inaccurate evaluation gives rise to spurious peaks in Fourier transform at low distances. By a trial and error procedure, μ_0 was best evaluated by a spline of three polynomial functions of 3^{rd} , 3^{rd} and 6^{th} degrees in the k ranges (2-10), (10-15) and (15-23) Å⁻¹, respectively as shown in Fig. (4.4 (dashed line in the inset curve)). After the evaluation of μ_0 we have to normalize the x-ray absorption coefficient to get the normalized EXAFS signal (Fig. 4.5) as given by equation

$$\chi(k) = \frac{\mu - \mu_1}{\mu_0} \tag{4.2}$$

where μ_1 is a Victoreen-type function with absolute values normalized to the absorption jump of the spectra. We considered μ_1 decreasing according to the theory (see Fig. 4.5, inset curve).

The EXAFS signals $k\chi(k)$ of CdTe at different temperatures are illustrated in Fig.



Figure 4.5. Normalized EXAFS oscillation $k^2 \chi(k)$. In the inset the edge jump of the spectra = 1.3.

(4.6). The effect of temperature is clear, the intensity of the EXAFS signal decreases as the temperature increases.



Figure 4.6. k $\chi(k)$ signals at k-edge of Cd at some selected temperatures.

4.2 Fourier Transform

4.2.1 The direct Fourier transform (k to r)

The contributions of each coordination shell have been isolated through the direct Fourier transform equation (4.3) of the $\chi(k)$ from the reciprocal (k) to the real (r) space.

$$F(r) = \int_{k_{min}}^{k_{max}} [k^n \chi(k)] W(k) \exp(2ikr) dk$$
(4.3)

where W(k) is a window function whose purpose is to reduce the spurious oscillations induced by the finite k range of the transform. The limits k_{min} and k_{max} are chosen in order to eliminate the low-k region (where the extraction of μ_0 is not so accurate and MS effects are strong) and the high-k region (where the signal to noise ratio is not sufficiently high). The weighting by the factor k^n is to balance the low and high k-regions of EXAFS signal. It is necessary that all EXAFS spectra are treated exactly with the same filtering procedure.

In all the analysis we used k^2 as a weighting factor, 10% damped Gaussian window function and k_{min} - k_{max} of 2 - 20 Å⁻¹. In Eq. (4.3), F(r) is a complex function and therefore it is composed of a real part [Re] F(r) and an imaginary part [Im] F(r) such that the modulus |F(r)| is:

$$|F(r)| = \sqrt{[ReF(r)]^2 + [ImF(r)]^2]}$$
(4.4)

Fig. (4.7) shows the modulus and the imaginary part of the Fourier transform F(r) of EXAFS signal of CdTe at selected temperatures. The contribution from the first three coordination shells of back scattering atoms around the absorbing atom is clear in the modulus F.T. (Fig. 4.7) where the first-shell peak is well isolated at all temperatures. It is important to mention that the distance r in the F.T. does not correspond to the real distance because of the presence of the phase shift $\phi(k)$ in the phase equation of the EXAFS signal which shifts the peaks position in the modulus of F.T. to lower values by about $0.2 \div 0.3$ Å. The crystallographic values of the first three shells are listed in table 4.1. In the Modulus Fourier transform the 1^{st} shell peak is weakly affected by increasing the temperature but the 2^{nd} and 3^{rd} shells peak strongly decrease when the temperature increases (Fig. 4.7).

If we consider only the SS contribution from the outer shells, the 2^{nd} (Cd-Cd) and 3^{rd} (Cd-Te) shells exhibit strong thermal disorder, equivalent to a strong uncorrelated thermal motion, while the first (Cd-Te) shell displays a weak thermal disorder, equivalent to a strongly correlated thermal motion.

4.2.2 Back Fourier transform (r to k)

For further analysis of each coordination shell, the contribution of a shell to the whole experimental EXAFS signal can be singled out by inverse (back) Fourier transform with window W'(k) as in Eq. (4.5). In order to do that the coordination shell must be well isolated in the direct Fourier transform (see Fig. 4.7).

$$\chi_s(k) = (2/\pi) \int_{r_{min}}^{r_{max}} [F(r)W'(k)k^n \exp(-2ikr)dr$$
(4.5)



Figure 4.7. Modulus (continuous line) and imaginary part (dashed line) of the Fourier transform of EXAFS signal at Cd k-edge EXAFS of CdTe at selected temperatures.

The back Fourier transform for a given shell $\chi_s(k)$ is a complex function and has real part $\chi_s(k)$ and imaginary part Im $\chi_s(k)$. The real part corresponds to EXAFS signal

Table 4.1. Crystallographic parameters of the first three coordination shells of the CdTe as calculated from the Rietveld refinement of the XRD patterns measured at RT.Lattice parameter a = 6.480 Å [103]

Shell	Ν	r [Å]	r[Å] [103]
1^{st}	4	2.8	2.806
2^{nd}	12	4.58	4.582
3^{rd}	12	5.37	5.373

can be written as:

$$Re\chi_s(k) = \chi_s(k) = A_s(k)\sin(\phi_s(k)) \tag{4.6}$$

where $A_s(k)$ and $\phi_s(k)$ are the amplitude and phase relative to this coordination shell. From the real and imaginary parts resulting from the back fourier we can calculate the backscattering amplitude and phase shift of this coordination shell as illustrated in the following equations:

$$A_s(k) = \sqrt{[Re\chi_s(k)]^2 + [Im\chi_s(k)]^2}$$
(4.7)

$$\phi_s(k) = \arctan[Re\chi_s(k)/Im\chi_s(k)]$$
(4.8)

Therefore the procedure of complex Fourier transform allows us to separately calculate the amplitude and phase of the filtered signal. The backscattering amplitude and phase shift of the first coordination shell in the CdTe was extracted experimentally by means of back fourier transform. The first shell contribution was singled out by using back fourier transform in the range of r from 1.5 to 3.3Å and 20% Hanning window. Fig. (4.8), shows the isolated EXAFS signal of the first coordination shell at selected temperatures.

4.3 Quantative Analysis procedures

Two different procedures were considered for the EXAFS data analysis on CdTe in order to obtain quantitative information.



Figure 4.8. The filtered EXAFS signal of the first coordination shell at selected temperature of CdTe.

The first procedure (phenomenological) consisted of the separate analysis of phase and amplitude of the filtered signal through the ratio method [9,24] taking the lowest temperature spectra as reference for scattering amplitudes, phase shifts and inelastic terms. The analysis of ratio method have been performed using the computer package EXTRA [102].

The second procedure (Theoretical) is based on the non-linear best fit of theoretical spectra (the backscattering amplitudes, phase shifts and inelastic terms were calculated by FEFF6 code [52])to the experimental spectra using Artemis graphical interface of FEFFIT [104].

Once the physical parameters $|f_i(k, \pi)|$, ϕ_i , S_0^2 and λ in EXAFS equation (2.22) are known, so the EXAFS signal $\chi_s(k)$ of a given shell can be analyzed to obtain the sought structural parameters: coordination number N_s , average position and MSRD of the distribution of distances, C_1 and C_2 , respectively and possibly higher order cumulants. There is also the possibility of analyzing contemporarily more shells where taking into account the importance of the multiple scattering effect and its contribution in the outer shell analysis (see Fig. 4.9).

4.3.1 ratio method

The ratio method [24] is suitable only for the well isolated first shell (see Fig. 4.9), where there is only Single scattering contribution and Multiple scattering effects are absent. It consists of a separate analysis of phase and amplitude of the filtered EXAFS signal taking the lowest temperature spectra as a reference for the physical parameters.

The main advantage of this method is the lack of theoretical inputs, since the physical parameters supposed to be identical in both samples are canceled. Amplitude and phase obtained through Eqns. (4.7, 4.8) for a given coordination shell can be expressed as a function of cumulants according the equations:

$$A(k) = (S_0^2/k) N |f(k,\pi)| e^{C_0 - 2k^2 C_2 + 2k^4 C_4/3}$$
(4.9)

$$\phi(k) = 2kC_1 - (4k^3C_3)/3 + \dots \tag{4.10}$$



Figure 4.9. Modulus of the Fourier transform of EXAFS signal at selected temperatures, where the selected grey area shows the range of Fourier back-transform for the 1^{st} shell analysis.

Phase analysis

By considering EXAFS signal at lowest temperature is a reference and at any other temperature is the sample which identified by the labels (r) and (s), respectively. If the phase shifts are the same $[\phi^s(k) = \phi^r(k)]$, they are eliminated in the difference between the total phases:

$$\Delta \phi = \phi^{s}(k) - \phi^{r}(k) = 2k\delta C_{1} - 4k^{3}\delta C_{3}/3 + \dots$$
(4.11)

where $\delta C_1 = C_1^s - C_1^r$, $\delta C_3 = C_3^s - C_3^r$, ...

By plotting $\Delta \phi/2k$ versus k^2 (see Fig. 4.10, Right panel); the intercept gives δC_1 and the slope is proportional to δC_3 , where any deviations from linearity is due to neglecting the influence of higher order odd cumulants.

Amplitude analysis

If the parameters $|f(k,\pi)|$, S_0^2 and λ of sample and reference are the same, so they are eliminated in the ratio between sample and reference amplitudes.

$$ln[A^{s}(k)/A^{r}(k)] = ln(N^{s}/N^{r}) + (C_{0}^{s} - C_{0}^{r}) - 2k^{2}\delta C_{2} + 2k^{4}\delta C_{4}/3 - \dots$$
(4.12)

where $\delta C_2 = C_2^s - C_2^r$, $\delta C_4 = C_4^s - C_4^r$,

In our case the ratio of the coordination numbers $N^s/N^r = 1$. By plotting $ln(A^s/A^r)$ versus k^2 (see Fig. 4.10, Left panel), the slope is proportional to δC_2 and also any deviations from linearity is due to neglecting the influence of higher order even cumulants. The ratio method results gives directly the relative values ($\delta C_n = C_n(T) - C_n(T_{ref})$) of the cumulants of the effective distributions [9,38].

Separate analysis of phases and amplitudes of the filtered signals of the CdTe first shell at different temperature has been performed taking the 19K spectra as a reference. The phase differences and logarithms of Amplitude ratios are plotted against k^2 as shown in Fig. (4.10). At each temperature, different plots of phase differences and logarithmics of amplitude ratios were obtained from different pairs of data files. For each set of spectra at each temperature, the fitting range was chosen as the k-range were the different plots were in agreement. The curves in Fig. (4.10) show a deviation from the expected regular behavior at lower and higher k-values; this is probably due to spurious effect of Fourier filtering.

From ratio method; the relative values of the first four EXAFS cumulants, $(\delta C_i(T) - C_i(19K), i = 1, 2, 3, 4)$ of CdTe have been obtained and shown in Fig.(4.11). The uncertainties expressed as standard deviations of the means by averaging the results for different spectra measured at the same temperature with two different references taken at 19K.



Figure 4.10. The separate analysis by the ratio method at selected temperatures (the reference temperature is taken at 19K).Left panel: logarithms of amplitude ratios plotted against k^2 . Right panel:phase differences(divided by 2k) plotted against k^2 .

Effective and Real distribution

The ratio method gives directly the relative values of the cumulants of the effective distribution of distances, δC_n . The relation between the effective P (r, λ) and the real distribution ρ (r, λ) is given by [9]:

$$P(r,\lambda) = \rho(r) e^{-2r/\lambda}/r^2$$
(4.13)

One disadvantage of the ratio method is related to the difficulty of taking into account the dependence of the mean free path λ on wave vector k, which introduces an uncertainty in the evaluation of cumulants of real distribution. In this case, λ was taken to be $9 \pm 3\mathring{A}$ and the error was propagated to the final values of the different cumulants of the real distribution.

The difference between real and effective distributions as shown in Eq. (4.13), is physically due to the progressive attenuation of the photoelectron spherical wave with distance: the low-r part of the real distribution has a higher weight than the high-r part.

Different analytical and numerical procedures have been proposed for connecting the parameters of the real and effective distributions, limited to the first cumulant [9,38] or extended to higher order cumulants [10]. Particularly simple approximate analytical expression have been worked out in Ref. [56] to evaluate the cumulants δC_i^* of the real distribution $\rho(r)$:

$$\delta C_i^* = \delta C_i + 2\delta C_{i+1} \left(\frac{1}{R} + \frac{1}{\lambda}\right), \ n = 1, 2, 3, \dots$$
(4.14)

The results obtained from the ratio method δC_i of the effective distribution were then corrected for the effects of the limited mean free path and the spherical nature of the photoelectron wave. The relative values of the real distribution, δC_i^* were obtained assuming $\lambda = 9 \pm 3$ Å. In Fig. (4.11), the obtained relative values of the the first four cumulants of the real distribution (δC_i^*) are represented together with relative values of the effective distribution δC_i .

The relevance of first cumulant correction, where the first cumulant of the effective distribution is smaller than the real distribution, is well known in literature and is clearly evident in Fig. (4.11). The difference between the second and higher order cumulants of the two distributions is instead quite small.

4.3.2 FEFF6-FEFFIT method

The input file for the FEFF6 [52] code was the set of atomic coordinates of the ZB structure. The code computed the EXAFS signal as the sum of all paths that contribute in a cluster of atoms and given by Eq. (4.15). Table (4.2) shows the scattering paths for CdTe within the third shell distance as calculated by FEFF6 code and Fig. (4.12) shows the schematic illustration of the scattering paths in CdTe zincblende structure and related to the same arrangement of the path index inside the table.

The backscattering amplitudes and phases of single and multiple scattering paths


Figure 4.11. Relative values of the first four cumulants of the effective distribution δC_i (open circles) and of the real distribution δC_i^* (black circles).

Table 4.2. The Scattering paths for CdTe calculated by FEFF6 code [52], where for every path, the table contains: a path index, the number of equivalent paths (degeneracy), an approximate half-path length R, % importance factor with respect to the first shell SS path, the total number of legs and a path description.

path index	degeneracy	r [Å]	% importance	nlegs	comment
1	4	2.80	100.00	2	SS 1^{st} shell
2	12	4.58	61.09	2	SS 2^{nd} shell
3	12	5.09	2.96	3	Triangular (MS)
4	24	5.09	12.37	3	Triangular (MS)
5	12	5.37	37.78	2	SS 3^{nd} shell

were calculated using the FEFF6 code [50, 105] where each path is expressed by an effective EXAFS $\chi_{\Gamma}(k)$ equation as (4.16):

$$\chi_{th}(k) = \sum_{\Gamma}^{allpaths} \chi_{\Gamma}(k)$$
(4.15)

$$\chi_{\Gamma}(k) = \frac{N_{\Gamma}S_0^2 F_{\Gamma}^{eff}(k)}{kr_{\Gamma}^2} \sin(2kr_{\Gamma} - \frac{4}{3}k^3C_3 + \phi_{\Gamma}^{eff}(k))e^{-2k^2\sigma_{\Gamma}^2 + \frac{2}{3}k^4C_4} \quad (4.16)$$

A non-linear fit of theoretical spectra calculated by FEFF6 to experimental spectra has been made using the FEFFIT code and its graphical interface Artemis [104]. For each path imported from the FEFF6 calculation there is a set of structural parameters, S_0^2 , δr , σ^2 and possibly E_0 , C_3 , or C_4 , whose values are optimized by a non-linear fitting routine. The maximum number M of independent parameters obtainable from the data must be consistent with the range of the EXAFS signal through the Nyquist theorem [106] as in Eq. (4.17).

$$M = \frac{2\Delta k\Delta r}{\pi} + 2 \tag{4.17}$$

where $\Delta k = k_{max} - k_{min}$ and $\Delta r = r_{max} - r_{min}$, are the intervals of the direct and inverse Fourier transforms, respectively. The theoretical method is applicable to both



Figure 4.12. Schematic illustration of the CdTe scattering paths calculated from FEFF6 code, represents the first three SS paths and two multiple scattering paths (triangular paths) as relevant to table 4.2. Black and gray circles represent the Cd and Te atoms, respectively.

single and multiple scattering contributions to EXAFS signal.

It is reasonable to use the same S_0^2 and E_0 (the difference between experimental and theoretical edge energy values) parameters for each path in FEFF calculation, to reduce the number of the free parameters and define the relations between the other variables.

The first step in the analysis is to examine the experimental data with the individual paths as computed by FEFF6 (see table 4.2) to notice the contribution of the paths to the experimental spectrum. The first shell has only contribution from the first Single scattering path (Cd-Te), for the second (Cd-Cd) and third (Cd-Te) shell; single and multiple scattering paths contributions should be taken into account.

The first shell was fitted in the r-space between $1.6\mathring{A} \div 3.2\mathring{A}$ and the best fit between the theoretical and experimental spectra is shown in Fig. (4.13). In the fitting procedure, there is a mismatch of the value of edge energy E_0 between theoretical and experimental energy scales; therefore in the first fitting trials the values of E_0 and S_0^2 were left as free parameters and the average values were calculated ($E_0 = 3.4$ eV and $S_0^2 = 1$) and maintained fixed in the further analysis.

The number of the free parameters were reduced to the first four cumulants, δr , σ^2 , C_3 and C_4 which parameterize the first-shell distribution of distances. The uncertainty of the results was estimated by a least squares minimization and comparing different



Figure 4.13. Modulus and imaginary part of EXAFS Fourier transform in the 1^{st} shell region at selected temperatures: experimental data (continuous line) and best fitting FEFF6 simulated signal (dash-bolded line)

files at the same temperature. This method takes into account the k-dependence of the mean free path λ and gives directly the absolute values of the cumulants of the real distribution.

The fitting procedure was applied at all temperatures from 19K to 300K and gave the first four cumulants of the real distribution of distances. For a comparison with the results obtained from ratio method, the relative values of cumulants have been calculated by taking the lowest temperature as a reference (see Fig 4.14). Fig. (4.14) shows that, the relative values of the cumulants of the real distribution from FEFF6-FEFFIT (full circles) were all relatively agreed with the results obtained from ratio method (open circles).

There are a disagreements between two methods in the comparison of the absolute values of the second cumulant, as shown in Fig. (4.15). The accuracy of the results depends on using suitable model in the simulation code and the possible of presence of a systematic errors in phases and amplitudes calculated by FEFF6 simulation code [104] should be kept in mind. For single temperature measurements, these errors should be summed to the other statistical and experiential sources of the uncertainty.

4.4 First Shell EXAFS Cumulants

Accurate relative values of the EXAFS cumulants were obtained for the first shell with a good agreement between the phenomenological (ratio-method) and Theoretical (FEFF6-FEFFIT method) procedures of data analysis (see Fig. 4.14). The relative values of the first four EXAFS cumulants of the real distribution, δC_i^* as obtained from ratio method are listed in table (4.3).

Fig. (4.14) shows that, the errors in the relative values of the cumulants have been obtained from the FEFF6 code were much larger than in the ratio method. This is related to the presence of systematic errors in the FEFF6 code calculation and the difficulties in controlling the way of the calculation and decreasing the errors during the simulation. The possibility of choosing the fitting range in the amplitude and phase



Figure 4.14. Relative values of the first four cumulants obtained from the first four cumulants obtained from the ratio method(open circles) and from abest fit to FEFF6 simulation (full circles)



Figure 4.15. Absolute values of the second cumulant obtained from the ratio method (open circles) through the Einstein model(dotted line) and from a best fit to FEFF6 simulation (full circles).

analysis in the ratio method (see Fig. 4.10) makes it the best way in giving more accurate values of cumulants rather than the FEFF6 code.

4.4.1 First Shell: Thermal expansion

As it was pointed out in Chapter 2, the average distance measured by EXAFS first cumulant, $C_1^* = \langle r \rangle = \langle |r_2 - r_1| \rangle$ is larger than the crystallographic distance between average positions measured by diffraction $R_c = |\langle r_2 - r_1 \rangle|$ due to thermal vibrations perpendicular to interatomic bond [58].

$$\langle r \rangle = R_c + \frac{\langle \Delta u_{\perp}^2 \rangle}{2R_c} + \dots$$
 (4.18)

Therefore, the thermal expansion measured by EXAFS is larger than the expansion measured by diffraction. The temperature dependent EXAFS first cumulant δC_1^* di-

T [K]	$\delta C_1^*[10^{-3}\text{\AA}]$	$\delta C_2^* [10^{-3} {\rm \AA}^2]$	$\delta C_3^* \; [10^{-4} \text{\AA}^3]$	$\delta C_4^* \; [10^{-6} \text{\AA}^3]$
19	0.01 ± 0.35	$0.007{\pm}~0.01$	0.002 ± 0.01	0.13 ± 0.01
25	0.37 ± 0.06	$0.09 \pm \ 0.03$	0.02 ± 0.002	0.78 ± 0.4
50	0.81 ± 0.06	$0.19 \pm \ 0.01$	0.03 ± 0.008	0.83 ± 0.01
75	1.52 ± 0.08	$0.47{\pm}~0.01$	0.08 ± 0.003	0.95 ± 0.2
100	1.99 ± 0.2	$0.89 \pm \ 0.02$	0.11 ± 0.02	1.7 ± 0.2
125	3.05 ± 0.12	$1.2{\pm}~0.006$	0.23 ± 0.01	0.61 ± 0.01
150	4.27 ± 0.16	$1.8 \pm \ 0.003$	0.38 ± 0.02	2.6 ± 0.5
200	6.78 ± 0.12	$2.9{\pm}~0.02$	0.73 ± 0.03	7.5 ± 0.5
250	8.62 ± 0.13	$3.9\pm$ 0.03	1.09 ± 0.03	5.7 ± 0.4
300	11.8 ± 0.29	5.2 ± 0.13	1.67 ± 0.01	14.6 ± 2.1

Table 4.3. Temperature dependence of the first four, C_i^* of the first coordination shell of CdTe as obtained through the ratio method analysis.

rectly measures the "true" bond thermal expansion and compared with the "apparent" bond expansion δR_c measured by Bragg diffraction as shown in Fig. (4.16).

The values of the δC_1^* of the real distribution have been obtained assuming a photoelectron mean free path $\lambda = 9 \pm 3$ [101] as shown in Fig. (4.16). The EXAFS bond expansion is positive over the entire temperature range while δR_c shows a negative thermal expansion (NTE) in the range from 0 to 70 K, also the positive expansion above 100K from diffraction is weaker than positive expansion measured by EXAFS.

This behavior of the positive expansion of the 1st shell average distance and macroscopic NTE from diffraction has been found in many other systems like Ge [36], CuCl [38], Cuprites Ag_2O and Cu_2O [22] and delafossites $CuScO_2$ and $CuLaO_2$ [12].



Figure 4.16. EXAFS thermal expansion from ratio method (full circles) is compared to the crystallographic expansion from Bragg diffraction (continuous line)

4.4.2 First Shell: Mean Square Relative Displacements

To a good approximation, EXAFS second cumulant C_2^* directly measures the MSRD of pairs of atoms parallel to the bond direction $(MSRD_{\parallel})$ [24]:

$$C_2^* \equiv \langle \Delta u_{\parallel}^2 \rangle = M S R D_{\parallel} \tag{4.19}$$

The temperature dependence of the parallel MSRD $\langle \Delta u_{\parallel}^2 \rangle$ is directly given by the relative values of the second cumulant δC_2^* . The temperature dependence of the perpendicular MSRD, is calculated from the difference $\delta C_1^* - \delta R_c$ (see Eq. 4.18) [24]. The *absolute* values of both parallel and perpendicular MSRDs are generally obtained by fitting a phenomenological correlated Einstein [66] or Debye [59] model to the slope of their experimental *relative* values. (see sec.2.5).

It would be physically sound to compare the $\langle \Delta u_{\perp}^2 \rangle$ with the $\langle \Delta u_{\parallel}^2 \rangle$, taking into account the fact that the perpendicular MSRD is a projection of relative motion onto a plane, while the parallel MSRD is a projection along the bond direction [65]. Fig. (4.17)



Figure 4.17. Temperature dependence of the Parallel MSRD $\langle \Delta u_{\parallel}^2 \rangle$ and of the halved perpendicular MSRD $\langle \Delta u_{\perp}^2 \rangle$ (full circles) and the dotted lines are the best fitting Einstein models.

shows the fitting of the correlated Einstein model (dotted lines) to the parallel and perpendicular MSRDs (full circles) of CdTe first shell, where a good correspondence of the model to their relative values of the temperature dependence is found. Therefore, the the $MSRD_{\parallel}$ and $MSRD_{\perp}$ absolute values of CdTe first shell were estimated and the corresponding Einstein frequencies were $\nu_{\parallel} \cong 3.92$ THz and $\nu_{\perp} \cong 1.92$ THz, respectively.

From Einstein frequencies of the parallel and Perpendicular MSRDs, the effective force constants k_{\parallel} and k_{\perp} , respectively, can be calculated by Eq. (4.20), and directly compared as shown in table (5.5) (more details in chapter 5).

$$k = 4\pi^2 \nu^2 \mu \tag{4.20}$$

where μ is the reduced mass. The k_{\parallel} and k_{\perp} values can be considered as a measure of the effective resistance against stretching and bending of the bond respectively, between two nearest-neighbor atoms embedded in a crystal. The effective k_{\parallel} and k_{\perp} force constant values of Cd-Te were about 3.76 and 0.9 (eV/Å²), respectively.



Figure 4.18. The temperature dependent the ratio between perpendicular and parallel MSRDs of CdTe where measure the anisotropy of the relative vibrations.

The large difference between $\langle \Delta u_{\perp}^2 \rangle$ and $\langle \Delta u_{\parallel}^2 \rangle$ is a clear indication of the anisotropy of relative vibrations. From the ratio of the perpendicular to parallel MSRDs we can calculate the anisotropy of the relative vibration, $\langle \Delta u_{\perp}^2 \rangle / 2 \langle \Delta u_{\parallel}^2 \rangle$. for a perfectly isotropic relative vibrations; the perpendicular MSRD should be exactly twice the parallel MSRD. The ratio are generally temperature dependent as shown in Fig. (5.5), it is customary to refer to their asymptotic values for $T \to \infty$ [22, 36, 38].

The asymptotic values can be obtained from the ratio of the effective force constant as in Eq. (5.5):

$$\xi = k_{\parallel}/k_{\perp} \tag{4.21}$$

The asymptotic value of anisotropy is more effective especially when the results are available only at low temperatures and/or the Einstein frequencies are high for a perfect isotropy [12], $\xi = 1$. The anisotropy asymptotic value of the CdTe was about 4.17 (eV/Å³).

4.4.3 First Shell: MSRDs and MSDs

The parallel MSRD, $\langle \Delta u_{\parallel}^2 \rangle$ and perpendicular MSRD, $\langle \Delta u_{\perp}^2 \rangle/2$ measured by EXAFS can be compared with the sum of the un-correlated parallel and perpendicular MSDs, U_{\parallel} and U_{\perp} , respectively of absorber and backscatter atoms from the refinement of Bragg diffraction patterns.

X-ray vibrational studies on (100) oriented CdTe crystals as a function of the temperature have been done by Horning et. al [107]. The temperature dependence its integrated intensities have been determined between 8K and 360K and analyzed with Debye model. From accurate temperature dependent diffraction measurements the MSDs values of Cd and Te atoms have been evaluated [107].

Due to cubic symmetry of CdTe lattice, atomic vibrations around equilibrium positions MSDs are isotropic: therefore, according to Eqs. (2.42, 2.42), the parallel and perpendicular MSD in any direction for both Cd and Te atom are given by:

$$\langle u_{\parallel}^2 \rangle = \langle u_{any}^2 \rangle, \tag{4.22}$$

$$\langle u_{\perp}^2 \rangle = 2 \langle u_{any}^2 \rangle \tag{4.23}$$

The difference between the MSRDs measured by EXAFS and the sum of uncorrelated MSDs obtained from diffraction (Fig. 4.19) allows to evaluate the degree of correlation of atomic motion both parallel and perpendicular to the bond direction. Fig. (4.19) shows that, the parallel correlation between Cd-Te atomic pairs is larger than its perpendicular correlation.

The parallel and perpendicular MSRDs can be decomposed into the sum of two un-correlated MSDs and displacement correlation function (DCF) as in Eqs. (2.44, 2.44). From the uncorrelated MSDs measured by diffraction, the lower $\langle \Delta u_2 \rangle_{low}$ and upper $\langle \Delta u_2 \rangle_{upp}$ bounds according to the Eqs. (4.25, 4.25) are corresponding to relative displacements of the two atoms perfectly in phase and perfectly in opposite of phase motion, respectively [22, 58]:



Figure 4.19. The comparison of the Parallel and perpendicular MSRD and the sum of uncorrelated MSDs [107] parallel to bond and perpendicular to bond for the Cd-Te atomic pair.

$$\langle \Delta u^2 \rangle_{low} = \langle u_1^2 \rangle + \langle u_2^2 \rangle - 2\sqrt{\langle u_1^2 \rangle \langle u_2^2 \rangle}, \qquad (4.24)$$

$$\langle \Delta u^2 \rangle_{upp} = \langle u_1^2 \rangle + \langle u_2^2 \rangle + 2\sqrt{\langle u_1^2 \rangle \langle u_2^2 \rangle}$$
(4.25)

The upper and lower bounds have been calculated from the absolute uncorrelated MSDs [107] of the Cd(1) and Te(2) atoms for CdTe at different temperatures and compared with both parallel and perpendicular MSRDs as shown in Fig. (4.20). Both parallel $\langle \Delta u_{\parallel}^2 \rangle$ and perpendicular $\langle \Delta u_{\perp}^2 \rangle$ MSRDs of CdTe do not exceed the lower and upper bounds, i.e. there are a phase relationship between the two atoms. Fig. (4.20) shows that, the $MSRD_{\parallel}$ is slightly larger than the lower bound but $MSRD_{\perp}$ is larger than lower bound. This means that, the relative motion of Cd and Te atoms is characterized by a strong positive correlation (two atoms move in-phase) along the bond direction than their perpendicular motion.



Figure 4.20. The calculated upper(full square) and lower (open square) bounds of the Cd(1) and Te(2) atoms for CdTe from the absolute uncorrelated MSDs [107]and compared with both parallel and perpendicular MSRDs at different temperatures.



Figure 4.21. EXAFS Third cumulant and the best fitting with the one-dimensional quantum theoretical model [67,72] (full circles), $|k_3|=2.05 \ eV/Å^3$ and classical fitting(open circles), $|k_3|=1.96 \ eV/Å^3$.

4.4.4 First Shell: Asymmetry of the distance distribution

The EXAFS third cumulant C_3^* measures the asymmetry of the distribution of distances. The absolute values C_3^* have been evaluated by fitting the temperature dependence of the relative values, δC_3 to the classical approximation or quantum treatment approach [67,72] as shown in Fig. (4.21). The third order one-dimensional force constant $|k_3| = 2.05 \text{ eV}/ \text{Å}^3$ evaluated from the best fitting of the quantum approach is a measure of the anharmonicity of the effective pair potential. From the second and third cumulants, the deviation from the gaussian shape of the real distribution at high temperature can be evaluated according to the relation; $C_3^*/(C_2^*)^{3/2}$ where measure the distribution asymmetry.

For a reliable determination of the C_1^* and then bond thermal expansion, by taking into account in the data analysis the asymmetry of the distribution of interatomic distances through the third cumulant, C_3^* parameter. The thermal expansion due to asymmetry of the one-dimensional EXAFS effective potential V_{eff} according to the



Figure 4.22. Thermal expansion from the asymmetry of V_{eff} [67,72](open circles) is compared to the true bond expansion of the average interatomic distance measured by EXAFS (full circles) and to the crystallographic expansion (continuous line)

first order term in the quantum treatment (see sec. 2.6.2) is given by [67]:

$$a = -\frac{3(\kappa_3)}{\kappa_0} C_2^*$$
 (4.26)

where $\kappa_0 = \kappa_{\parallel} = \mu \omega^2$ the second order force constant [108]. Fig. (4.22) shows that, the thermal expansion obtained from δa is different from the crystallographic thermal expansion, δR_c as well as EXAFS first cumulant, δC_1^* .

The thermal expansion according to the first order term in the classical approximation (see sec. 2.6.1), has been evaluated from the third cumulant by the relation $\delta C_1^* = C_3^*/2C_2^*$. Fig. (4.23) shows the thermal expansion calculated by the classical and quantum approaches, where the difference between two approaches become lower and behaves classically at higher temperature.

The comparison between the relative values of the thermal expansion obtained from EXAFS first cumulant δC_1^* and relative values evaluated from the classical and quantum approaches have been shown in Fig. (4.24). In Fig. (4.23), its clear that the relative values of the thermal expansion obtained from the third cumulant by two



Figure 4.23. The thermal expansion calculated from the third cumulant on the classical approximation, $C_3^*/2C_2^*$ (full circles) and quantum treatment, $-\frac{3\kappa_3}{\kappa_0}C_2^0$ (open circles) at the lowest order terms

different approaches do not agree with the relative value of the thermal expansion of the first cumulant δC_1^* .

We can concluded that, there is no a priori relation between thermal expansion and third cumulant, so that the thermal expansion measured by different approaches from third cumulant cannot be considered as a measure of thermal expansion, while the true bond thermal expansion is still measured by the temperature variation of the EXAFS first cumulant. The one-dimensional EXAFS effective potential is in principle a temperature dependent in both position and shape.

Then, the thermal expansion (first cumulant) is consider as a joint effect of asymmetry (third cumulant) and shift of the effective potential, where the potential shift is related to vibrations perpendicular to the bond [10].



Figure 4.24. The relative values of the thermal expansion obtained from classical(full square) and quantum(full circles) approach and compared with the realative values of the EXAFS first cumulant cumulant" true expansion, δC_1^* (open circles)

4.5 Outer Shell Analysis

In the 2^{nd} and 3^{rd} shells analysis, it is important to take into account both single and multiple scattering contributions to EXAFS signal as clear in Fig. (4.9). EXAFS signal in Fig. (4.7) shown that, the signal to noise ratio at high temperatures becomes large, then the Fourier transform from the outer shells is much low. The multiple scattering is effect strongly in the phase analysis (first and third cumulants) than Amplitude analysis (Second cumulant).

4.5.1 FEFF6-FEFFIT method

The 2^{nd} and 3^{rd} shell analysis have been done using FEFF6-FEFFIT code [52, 104], where allows to take into account the multiple scattering contributions to obtained the best fit of the calculated EXAFS signal to the experimental data. All scattering paths calculated by FEFF6 within the two shells were described in table (4.2). To define several free parameters in the fitting procedure of the FEFF6 code were prevented to obtain a stable fit of the calculated signal. Then to obtain the best fit and stable results, the free parameters should be reduced as much as possible.

The 2^{nd} and 3^{rd} shells were fitted in the r-space between 3.5 Å to 5.7 Å as shown in Fig. (4.25). The fitting procedure was performed such as for the first shell, the average values of E_0 and S_0^2 were calculated 4.5 eV and 1 respectively, in a first trial analysis and maintained fixed in a further analysis. The important scattering paths calculated by FEFF6 code within the two shells were included in the fitting procedure. For Single scattering paths of 2^{nd} and 3^{rd} shells, the second cumulants were considered as free parameters. The second cumulant of (nonlinear) MS paths were constrained to a Debye model with $\theta_D = 170K$, where θ_D is the average value of x-ray and specific heat Debye temperature. The thermal expansion of all SS and MS paths in the outer shells was described by a unique fitting coefficient parameter ALPHA.

From the best fitting of the calculated EXAFS "physical parameters" to the experimental data, the parallel MSRD of 2^{nd} and 3^{rd} shells have been directly obtained from the second cumulant. According to the discussion in sec. (4.3.2), of the first shell, the absolute values of FEFF6-FEFFIT are not significant with an accuracy sufficient and not reliable enough for the aim of this work, then the relative values were then considered as shown in Fig. (4.27).

4.5.2 Ratio method

In the ratio method, it is possible to perform the amplitude analysis of the 2^{nd} and 3^{rd} shell but it is difficult to perform the phase analysis due to the importance of the multiple contribution and the difficulty to choice the suitable fitting interval. The amplitude analysis have been performed for the second and third shell using 19K spectra as a reference, the relative values of the second cumulant, δC_2 have been obtained as in Fig. (4.27). The relative errors have been evaluated by averaging the different measurements at the same temperature. The parallel MSRD of 2^{nd} and 3^{rd} shells are shown in Fig. (4.26), where the absolute values have been obtained by fitting



Figure 4.25. Modulus and imaginary part of Fourier transform of EXAFS signal (continuous lines) and best fitting signals(dash-bolded lines) of the outer shells at some selected temperatures on CdTe.

Shell	frequency(THZ)	$k_{\parallel}(eV/\mathring{A}^2)$
First	3.92	3.76
Second	1.93	0.91
Third	1.77	0.77

Table 4.4. Einestien [66] frequencies and the values of the effective force constants k_{\parallel} of the first three shells of the CdTe from ratio method.



Figure 4.26. The parallel MSRD for the First three coordination shells of CdTe given by ratio method and the best fitting Einstein models (dotted lines) as given by ratio method.

Einstein model [66] and compared with the absolute values of the first shell. Table (4.4), summarizes the best-fitting Einstein frequencies of three coordination shells of CdTe.

The relative values of the second cumulant, δC_2 of the 2^{nd} and 3^{rd} shells were evaluated with a good agreement between the ratio method and FEFF6-FEFFIT method as shown in Fig. (4.27).

The correlation of atomic motion parallel to the bond direction can be calculated for the outer shells according to Eq. (4.23). The $MSRD_{\parallel}$ obtained from EXAFS of the 2nd and 3rd shells were compared with the MSDs measured by diffraction of Cd



Figure 4.27. The relative values of the second cumulant obtained from the FEFF6-FEFFIT and ratio method of the 2^{nd} and 3^{rd} shells of CdTe.



Figure 4.28. Parallel MSRDs of the 2^{nd} and 3^{rd} shells as given from FEFF6-FEFFIT of CdTe and the comparison with the sum of uncorrelated parallel MSDs [107] of the Cd+Te and Cd+Cd atomic pairs (stars).

and Te atoms [107] and shown in Fig. (4.28). The second shell $MSRD_{\parallel}$ is significantly lower than the sum of the uncorrelated MSD_{Cd+Cd} , i.e characterized by high degree of correlation of parallel relative motion (see Fig. 4.28).

The third shell, $MSRD_{\parallel}$ slightly lower than the value of MSD_{Cd+Te} , i.e the parallel relative motion are partially correlated but less than the correlation of the second shell, where the degree of correlation governing the atomic motion and decreases rapidly with increasing the distance between the absorber-backscatter pair.

The average thermal expansion of the second and third shell distances obtained through the nonlinear best fit (FEFF6-FFEFFIT) procedure is positive as shown in Fig. (4.29) and considerably lower than the 1^{st} shell bond expansion (Fig. 4.16). we should take into account that the ALPHA parameter has not a physical meaning, science it does not account for possible difference between the local expansion of the second and third shell. In the fitting procedure, the third cumulant was not included and the ALPHA parameter was generally increased with temperature, which is highly correlated with E_0 parameter.



Figure 4.29. The average thermal expansion obtained from the FEFF6-FEFFIT analysis of the outer shells(full circles) and compared to the crystallographic expansion(line)

The same conclusion have been obtained in the case of outer shell of CuCl [38] and also for Cu [24], which a reliable information on outer shells could be obtained only concerning the second cumulants.

In the outer shell analysis after a large number of trials and inserting more fitting parameters: third cumulants or different expansions for each shell was led to prohibitively large correlations between the parameters and spoiled the results of any reasonable meaning.

Chapter 5

Discussion

In this final chapter, a critical comparison of the EXAFS results for Ge, CdTe and CuCl zincblende crystals is done. The values of the relevant parameters measured by EXAFS for CdTe are intermediate between the corresponding values previously found for Ge and CuCl. A correlation can be established between NTE properties and several quantities measured by EXAFS; Bond thermal expansions, parallel and perpendicular MSRDs and anisotropy of relative atomic vibrations. The effective force constants obtained from EXAFS results of CdTe are also compared with the short range force constants of the Valence Force Field, VFF model.

5.1 Comparison EXAFS-XRD: Thermal Expansion

From the comparative study of EXAFS and Bragg diffraction results, original information can be obtained on the origin of negative thermal expansion of the crystals. Diffraction is sensitive to long range order and provides information on average thermal parameters, while EXAFS is sensitive to the local order, and provides information about local thermal properties. Recently, the difference between the thermal expansions of the interatomic distances measured by EXAFS and by Bragg diffraction has been experimentally detected. This difference is due to the effect of the relative vibrations in the plane perpendicular to the bond direction and can be connected to the tension effect, responsible for NTE.

5.1.1 EXAFS first cumulant and crystallographic expansion

Let us focus here on the nearest-neighbor bond distance of Ge, CdTe and CuCl crystals, where the strength and temperature interval of NTE increases with increasing bond ionicity. For a simple crystal structure like zincblende, the expansion of the distance between average positions of any atomic pairs is proportional to the expansion of the lattice parameter measured by Bragg diffraction. EXAFS measures the true bond thermal expansion from the temperature variation of the first cumulant, δC_1^* , while diffraction measures the crystallographic expansion δR_c (see sec. 2.4).

Fig. (5.1) shows the nearest neighbor thermal expansion measured by Bragg diffraction (continuous line) and by EXAFS (full circles) in Ge [36], CdTe and CuCl [38]. The coefficient of thermal expansion, $\alpha = (dR_c/dT)/R_c$ measured by Bragg diffraction is strongly temperature dependent. While the bond thermal expansion coefficient, $\alpha_{Bond} = (dC_1^*/dT)/C_1^*$ measured by EXAFS is monotone and its average value can be well defined (see table 5.1).

CuCl exhibits the strongest NTE; the distance between average positions of nearest neighbor atoms undergoes negative expansion up to 100K ($\alpha_{low} \simeq -0.8 \times 10^{-5} K^{-1}$) and positive expansion above 100K ($\alpha_{max} \simeq 1 \times 10^{-5} K^{-1}$), while the average distance measured by the first EXAFS cumulant undergoes a positive and stronger expansion at all temperatures ($\alpha_{bond} \simeq 4.3 \times 10^{-5} K^{-1}$).

We assume here that the linear coefficient of lattice thermal expansion at low temperatures, α_{low} measured by Bragg diffraction is a measure of the strength of NTE; its absolute value increases when going from Ge to CdTe to CuCl as shown in table (5.1). The coefficient of bond thermal expansion measured by EXAFS α_{Bond} is always positive; its average value increases when the NTE strength increases. Therefore, the stronger is the lattice NTE measured by diffraction, the stronger is the bond PTE



Figure 5.1. First shell bond thermal expansion from EXAFS (full circles) compared to the crystallographic expansion from Bragg diffraction (continuous line) for Ge, CdTe and CuCl crystals.

Table 5.1. Crystallographic linear thermal expansion coefficient at low temperature" α_{low} ", average coefficient of bond thermal expansion from EXAFS" α_{Bond} ", third order force constant k_3 , third cumulant C_3^* at 0K and skewness parameter $\beta = C_3^*/(C_2^*)^{3/2}$ for the first shell of Ge, CdTe and CuCl crystals.

	$lpha_{low}$	α_{Bond}	k_3	C_3^*	$\beta = C_3^* / (C_2^*)^{3/2}$
	$(10^{-6}K^{-1})$	$(10^{-6}K^{-1})$	$eV/({ m \AA}^3)$	$(10^{-5}K^{-1}\mathring{A}^3)$	at 300 K $$
Ge [36]	-0.05	8	-4.8	0.3	0.15
CdTe	-3	18	-2.05	0.44	0.25
CuCl [38]	-8	43	-1.2	2.9	0.61

measured by EXAFS. The difference $\alpha_{Bond} - \alpha_{low}$ increases with increasing the bond ionicity from Ge to CdTe to CuCl (see Fig. 5.1).

5.1.2 EXAFS third cumulant

EXAFS third cumulant, C_3^* measures the distribution asymmetry and is directly connected to the anharmonicity of the one-dimensional effective pair potential. Its presence in EXAFS analysis is necessary to obtain accurate values of distances and mean square relative displacements. Fig. (5.2) shows the temperature dependence of the EXAFS third cumulant of the first shell of Ge, CdTe and CuCl.

According to a perturbative quantum approach [67, 72], the 3^{rd} cumulant can be expressed to first order as:

$$C_3^* = \frac{k_3(h\nu_E)^2}{2k_0^3} \frac{z^2 + 10z + 1}{(1-z)^2}$$
(5.1)

where ν_E and k_0 are the Einstein frequency and effective bond stretching force constant, determined from the second cumulant (see table 5.3) and $z = \exp(-h\nu_E/k_BT)$. Fig. (5.2), shows that the third cumulant of Ge, CdTe and CuCl are in agreement with the behavior of the one-dimensional quantum model of Eq. (5.1).



Figure 5.2. Temperature dependence of the EXAFS third cumulant (full circles). The dotted lines are the best fitting according to Eq. (5.1); zero-point values are clearly visible for Ge and CdTe.

In the classical approximation to first order (see sec. 2.6.1), the third cumulant depends quadratically on temperature, the classical approximation can be adequate at high temperature but it fails at low temperature due to the presence of zero point vibrations of quantum origin. The quantum treatment (see sec. 2.6.2) accounts for the zero point contributions, the nonzero absolute values of C_3^* at 0K are about 0.3, 0.44 and 2.9 (×10⁻⁵Å³) for Ge [36], CdTe and CuCl [38], respectively. The good agreement with the quantum model represents a self-consistency test of the data analysis and suggests that the shape of the effective pair potential is insensitive to temperature; a similar result was found for copper [24].

From the best fit with the one-dimensional quantum model, the third order effective force constant, k_3 of Ge, CdTe and CuCl have been obtained and are listed in table 5.1. The 3^{rd} cumulant depends on the anharmonicity of the effective pair potential, while the zero-point value of C_3^* increases, the magnitude of k_3 decreases from Ge to CdTe to CuCl as shown in table (5.1). The increase of α_{Bond} and the decrease of α_{low} are accompanied by the decrease of $|k_3|$; i.e. looser bond.

Actually, the potential anharmonicity jointly effects the 2^{nd} and 3^{rd} cumulants. A direct evaluation of its effect can be obtained by considering the asymmetry of the distribution of distances. The asymmetry of distribution (deviation of the real distribution from the gaussian shape) is measured by the skewness parameter $\beta = C_3^*/(C_2^*)^{3/2}$. The values of β at 300K are listed in table. (5.1). The asymmetry parameter, say the asymmetry of the first shell distribution increases from Ge to CdTe to CuCl.

A numerical evaluation of the asymmetry parameter of the real distribution and its comparison with the experimental values for germanium [10] suggested that the main contribution to the experimental third cumulant comes from the crystal anharmonicity, and the contribution of the vibrations perpendicular to the bond is negligible.

5.1.3 Thermal expansion from potential anharmonicity

Once k_3 is known, the net thermal expansion due solely to the asymmetry of the effective pair potential can be calculated, according to Frenkel and Rehr quantity $a = -3k_3C_2^*/k_0$ [67]. The relative values $\delta a = a(T) - a(T = 19K)$ have been compared in Fig. (4.22) with the crystallographic expansion, δR_c and with the expansion of the 1st EXAFS cumulant, δC_1^* . For CdTe in Fig. (4.22), δa and the crystallographic thermal expansion clearly disagree and both are weaker than the true bond expansion measured by δC_1^* . Similar results have been obtained for copper [37] as well as for Ge [36] and CuCl [38]. Then, crystallographic thermal expansion, δR_c cannot in general be obtained from the asymmetry of the effective potential and it seems that there is no way for obtaining the crystallographic expansion directly from an EXAFS experiment.

The difference between thermal expansions measured by the first and the third cumulants has been explained in terms of a rigid shift of the effective pair potential [35, 109, 110]. In two-atomic molecules, the thermal expansion is solely due to anharmonicity of the pair potential, i.e to the asymmetry of the distribution and can be evaluated equivalently from δC_1^* or from the second and third cumulants through the quantity δa . For a crystal, the effective EXAFS pair potential depends on the statistically averaged behavior of all atoms in the crystal and can in principle be temperature dependent both in position and shape [74]. While no relevant variations of shape have been experimentally detected up to now, while a shift of the minimum position has been observed for all investigated systems. The bond thermal expansion can thus depend on the shift of the minimum of the effective pair potential, corresponding to a shift of the maximum of the distribution of distances.

The temperature dependence of the first shell parameters determined experimentally (average distance, parallel and perpendicular MSRDs, third cumulant) for copper have been satisfactorily reproduced by path-integral Monte Carlo (PIMC) calculations [14] performed with a many-body potential. The agreement between PIMC and EXAFS confirmed that, the bond thermal expansion cannot be solely obtained from the asymmetry of the effective potential through the third cumulant. The inadequacy of the one-dimensional model plays a role in this failure, the local mechanism of bond thermal expansion being more complicated, and not simply explainable in terms of the anharmonicity of the EXAFS effective potential.

In conclusion, the bond thermal expansion (first cumulant) is a joint affect of asymmetry (third cumulant) and shift of the effective potential. A relevant contribution to the potential shift is related to vibrations perpendicular to the bonds [10]. EXAFS PTE which directly reflects the effect of bond stretching, is also connected with the positive shift of the minimum of the effective potential, which in turn is connected to the perpendicular MSRDs.

5.1.4 Thermal expansion of outer shells

The average thermal expansions of the second and third shell distances obtained through the nonlinear FEEF-fit procedure for CdTe (see Fig. 4.29) and CuCl [38] were found to be positive, although their values are lower than the values measured for the nearest neighbors distance. However, the ALPHA parameter measures the average thermal expansion of the outer shells in the FEFFIT code has a limited physical meaning; it does not account for possible differences between the local expansions of the second and third shell; besides the third cumulants were not included in the fitting procedure.

Recently, the PIMC calculations for the outer shells of copper [37] shown that, the the contribution due to asymmetry is much weaker than for the first shell and the expansion is nearly completely accounted for by the shift of the maximum of distribution. The neglect of the third cumulant should not be a source of large error in the evaluation of thermal expansion even for the outer shells of CdTe.

	k_{\parallel}	k_{\perp}	$\xi = k_\parallel/k_\perp$
	$eV/(\mathring{A}^2)$	$eV/(\mathring{A}^2)$	
Ge [36]	8.05	2.89	2.94
CdTe	3.8	0.9	4.17
CuCl [38]	1.4	0.26	5.38

Table 5.2. Comparison of three crystal with the diamond-zincblende structure. 2^{nd} order effective force constants k_{\parallel} , k_{\perp} and anisotropy parameter ξ

5.2 Comparison EXAFS - XRD: Thermal Factors

Bragg diffraction measures the average of the square of the absolute displacements of single atoms (MSDs). EXAFS measures the average square of the relative displacement of a couple of atoms (MSRDs). The parallel and perpendicular MSRDs have been obtained from the EXAFS second cumulant and from the difference $\delta C_1^* - \delta R_c$, respectively. Fig. (5.3) shows, the temperature dependence of both parallel and perpendicular MSRDs, $\langle \Delta u_{\parallel}^2 \rangle$ and $\langle \Delta u_{\perp}^2 \rangle/2$, respectively and the best fitting Einstein model of Ge, CdTe and CuCl. In Fig. (5.3), both $\langle \Delta u_{\parallel}^2 \rangle$ and $\langle \Delta u_{\perp}^2 \rangle/2$ as well as their difference $\langle \Delta u_{\perp}^2 \rangle/2 - \langle \Delta u_{\parallel}^2 \rangle$, increase going from Ge to CdTe to CuCl. The difference between the parallel and perpendicular MSRDs is an indication of the anisotropy of relative vibrations.

The Einstein frequencies ν best fitting the parallel and perpendicular MSRDs can be connected to effective force constants k_{\parallel} and k_{\perp} , respectively. Table (5.2) shows the calculated values of k_{\parallel} and k_{\perp} of Ge, CdTe and CuCl. Their values can be considered as a measure of the effective resistance against stretching and bending, respectively, of the bond between two nearest neighbors atoms embedded in a crystal.

The parallel MSRDs of the first three coordination shells of Ge [36], CdTe and CuCl [38] are compared in Fig. (5.4). The CdTe behavior is again intermediate between Ge and CuCl. In CuCl, the values of $MSRD_{\parallel}$ of the three coordination shells are



Figure 5.3. Temperature dependence of the Parallel MSRD $\langle \Delta u_{\parallel}^2 \rangle$ and of the halved perpendicular MSRD $\langle \Delta u_{\perp}^2 \rangle/2$ (full circles) and the dotted lines are the best fitting Einstein models for Ge, CdTe and CuCl crystals.

		Einestien frequencies		$k_{\parallel}(eV/\mathring{A}^2)$		
Shell	Ge	CdTe	CuCl	Ge	CdTe	CuCl
First	7.5	3.92	3.93	8.06	3.76	1.44
Second	3.9	1.93	1.66	2.18	0.86	0.36
Third	3.48	1.77	1.77	1.73	0.77	0.29

Table 5.3. The Einstein frequencies, ν_{\parallel} (THz) and the parallel effective force constant, k_{\parallel} of the first three coordination shells of Ge [111], CdTe and CuCl [38]

higher than in Ge and CdTe, i.e. CuCl is characterized by a much stronger thermal disorder than Ge and CdTe.

The Einstein frequencies ν_{\parallel} of the first three coordination shells are listed in table (5.3), allows us to compare the effective stiffness of bond extended up to the third shell corresponding to the force constant $k_{\parallel} = 4\pi^2 \nu_{\parallel}^2 \mu$ (μ is the reduced mass). The calculated values of k_{\parallel} of the first three coordination shells of Ge, CdTe and CuCl are listed in table (5.3). For each crystal, k_{\parallel} decreases with increasing the interatomic distance from the first to third shell, also decreases in going from Ge to CdTe to CuCl. However the frequencies of CuCl and CdTe are comparable, while k_{\parallel} smaller for CuCl than CdTe due to the difference of their atomic mass. k_{\parallel} depends on the reduced mass; where CuCl is lighter than the CdTe.

5.2.1 Anisotropy: MSRDs - MSDs

The anisotropy of thermal factors can be relevant to the explanation of NTE, since it can be connected to the extent of vibrations perpendicular to the bond. Anisotropy of relative vibrations can be measured by the ratio $\langle \Delta u_{\perp}^2 \rangle / 2 \langle \Delta u_{\parallel}^2 \rangle$ for the MSRDs of EXAFS and by the ratio U_{\perp}/U_{\parallel} for the absolute atomic vibrations, MSDs of diffraction. These ratios are generally temperature dependent. It is worth to notice that



Figure 5.4. Parallel MSRDs of the first three coordination shells of Ge [36], CdTe and CuCl [38] and the best fitting Einstein model (dot line).
thermal factors of EXAFS and diffraction have different anisotropy properties. In the delafossite and cuprite structures NTE has been connected to the anisotropy of the thermal factors of central atoms in linear A-B-A links measured by diffraction.

Some crystals with the delafossite structure, e.g. $CuMO_2$ (M= Al, Sc, In, La) undergo NTE along the c-axis in a non-negligible temperature interval [112]. The linear O-Cu-O links are parallel to the c-axis; according to diffraction, the NTE along c axis is due to the contraction of the distance between Cu and O average positions, and is accompanied by the anisotropy of the Cu thermal ellipsoids, the amplitude of vibration being stronger in the plane perpendicular to the c-axis.

A linear O-M-O link is also present in the crystals of Cuprite structure, M_2O (M= Ag, Cu), where each M atom is linearly coordinated to two O atoms, while each O atom is tetrahedrally coordinated to four M atoms. The NTE of the cuprite framework structure is related to the vibrations of M atoms perpendicular to the O-M-O links. Disk-shaped thermal ellipsoids for the central M atoms of O-M-O links in cuprites have been measured by diffraction [22].

The anisotropy of *relative* vibrations seems to be more relevant than the anisotropy of *absolute* vibrations. In delafossites, the MSRD anisotropy of the Cu-O pairs is larger in CuScO₂ than in CuLaO₂, say in the system affected by the larger NTE, while the anisotropy of the Cu ellipsoid is larger in CuLaO₂ than in CuScO₂ [34]. In cuprites, the anisotropy of the relative M-O vibrations measured by the MSRD is much larger than the anisotropy of the absolute motion of metal atoms [18].

In the diamond-zincblende systems, the MSDs from diffraction are isotropic for symmetry reasons. The ratio between MSRDs is thus particularly useful for studying NTE in the diamond-zincblende crystals. In Fig. (5.3) clear that Ge, CdTe and CuCl have perpendicular MSRDs ($\langle \Delta u_{\perp}^2 \rangle/2$) significantly larger than the parallel MSRDs ($\langle \Delta u_{\parallel}^2 \rangle$) reflecting a strong perpendicular to parallel anisotropy of relative vibrations. Fig. (5.5), shows the comparison of the ratio between perpendicular and parallel MSRDs ($\gamma = \langle \Delta u_{\perp}^2 \rangle/\langle \Delta u_{\parallel}^2 \rangle$) of Ge [36], CdTe and CuCl [38]. The high temperature



Figure 5.5. Temperature dependence of the ratio $\gamma = \langle \Delta u_{\perp}^2 \rangle / \langle \Delta u_{\parallel}^2 \rangle$ between perpendicular to parallel MSRDs of Ge [36], CdTe and CuCl [38]. for perfect isotropy the ratio should be $\gamma = 2$.

value of γ increases from about 6 in Ge to about 11 in CuCl. The CdTe behavior is intermediate between Ge and CuCl; the stronger lattice NTE is the larger difference between perpendicular and parallel MSRDs, i.e. larger anisotropy.

A temperature independent measure of the anisotropy is given by the ratio $\xi = k_{\parallel}/k_{\perp}$ (see sec. 2.4.3). The anisotropy parameter ξ of Ge, CdTe and CuCl are listed in table (5.2): again one can see that, the anisotropy increases going from Ge to CdTe to CuCl.

By a comparison with the results previously found for Ge and CuCl (see Fig. 5.5), the intermediate results obtained for CdTe confirm that the stronger NTE is accompanied by a larger anisotropy of relative atomic vibrations.

5.3 Correlation effects: EXAFS versus XRD

The fact that, the anisotropy of the MSRDs is more relevant for NTE than the anisotropy of the MSDs related to the correlation between the atomic vibrations. The



Figure 5.6. The parallel MSRDs of the first three coordination shells compared with the sum of parallel MSDs of Ge [61].

type of correlation of atomic vibrations is important for a given interatomic bond to show apparent NTE. Two atoms have full parallel correlation along a given direction, if their vibrations are perfectly in phase. Similarly, if the atoms are vibrating perfectly in opposite of phase then they have full antiparallel correlation. The MSRDs is small if the atoms have parallel correlation, is large if the atoms have antiparallel correlation.

The extent of correlation of vibration can be evaluated by measuring how much the MSRDs is smaller than the sum of the uncorrelated MSDs of the two atoms. EXAFS parallel MSRDs of Ge, CdTe and CuCl have been compared with the sum of uncorrelated parallel MSDs measured by diffraction. Fig. (5.6) shows the parallel MSRD of the first three coordination shells of Ge compared with twice the MSD (available only at 300K) [61]. The degree of correlation is strong for the first shell, weaker for the second and third shells. For the first shell of Ge there is considerable degree of correlation also in the perpendicular direction.

Fig. (5.7) shows the parallel MSRDs of the first three coordination shells of CdTe compared with the sum of parallel MSDs (Cd+Te, Cd+Cd), available in the full T



Figure 5.7. The parallel MSRDs of the first three coordination shells compared with the sum of parallel MSDs of CdTe.



Figure 5.8. The parallel MSRDs of the first three coordination shells compared with the sum of parallel MSDs of CuCl [38].

range [107]. The relative vibrations parallel to the bond are strongly correlated for the first shell less for the second shell and still less for the third shell. For the first (Cd-Te) shell, relative vibrations have a considerable degree of correlation also in the perpendicular direction as found in Ge. Cd and Te nearest neighbors are vibrating strongly in-phase parallel to the bond direction and partially in-phase in the perpendicular direction (see Fig. 4.20).

Fig. (5.8) shows the parallel MSRDs of the first three coordination shells of CuCl compared with the sum of the parallel MSDs (Cu+Cl and Cu+Cu), available only at 300K. The parallel relative motion of the first (Cu-Cl) and second (Cu-Cu) shell atomic pairs is characterized by a quite strong correlation but third shell (Cu-Cl) motion appears instead uncorrelated. For the first shell of CuCl it was found that, the relative atomic motion is highly correlated along the bond direction but it is almost un-correlated in the plane perpendicular to bond [38].

5.3.1 Connection: MSRDs - NTE properties

The phenomenological interpretation of NTE is based on the separation of bond stretching and tension effects. The comparison of different crystals sharing the same structure (Ge, CdTe and CuCl), shows that a correlation can be established between NTE properties and some quantities measured by EXAFS, such as bond thermal expansion, perpendicular MSRD and anisotropy of relative vibrations. The positive bond expansion is directly connected to the bond-stretching effect, while the perpendicular MSRD can be connected to the tension effect, the responsible for NTE. An alternative way of monitoring the tension effect is to consider the anisotropy of atomic vibrations.

The effective bond stretching and bond bending force constants, k_{\parallel} and k_{\perp} have been calculated for the first shell of Ge, CdTe and CuCl and are compared in table. 5.2 with the corresponding quantities measured for other families of NTE crystals (cuprites and delafossites structure). There are some general common features in these results; the nearest neighbor bond thermal expansion from EXAFS is always positive. Within each family of iso-structural compounds; (i) the stronger is the apparent NTE, the

Table 5.4. Force constants k_{\parallel} , k_{\perp} and anisotropy parameter $\xi = k_{\parallel}/k_{\perp}$ for selected crystals. The last two lines list the thermal expansion coefficient at low temperature, α_{low} measured by Bragg diffraction and average coefficient of bond thermal expansion from EXAFS, α_{Bond} .

	Cu	Ge	CdTe	CuCl	Cu_2O	Ag_2O	$CuScO_2$	$CuLaO_2$
k_{\parallel}	3.2	8.05	3.76	1.4	11.6	5.9	15.5	24.2
k_{\perp}	2.72	2.9	0.9	0.3	2.9	0.5	2.6	1
ξ	1.17	2.9	4.17	4.7	4.0	11.8	6.0	24.2
$\alpha_{low}(10^{-6}K^{-1})$	-	-0.05	-3	-8	-2.4	-10.4	-2.3	-5.5
$\alpha_{bond}(10^{-6}K^{-1})$	-	8	18	43	7.5	35	9	16

larger is the positive bond expansion accompanied by stronger anisotropy ξ of relative vibration. (ii) a stronger bond PTE, the stronger lattice NTE are accompanied by a smaller value of k_{\parallel} corresponding to looser bond, and a smaller value of k_{\perp} suggesting direct correlation between perpendicular MSRD and tension effects responsible of NTE.

The fact that stronger negative lattice expansions measured by diffraction are accompanied by stronger positive bond expansions for all studied crystals can at first sight appear puzzling. It is however reasonable that the stretching and tension effects are in some way positively correlated. The increase of the NTE strength corresponds to larger perpendicular vibrations and stronger perpendicular to parallel anisotropy, accompanied by a loosing and a position shift of the effective potential that favors the positive bond expansion. Otherwise, stated when the anisotropy of relative vibrations increases, the tension effect giving rise to NTE increases; in relatively open structures like diamond-zincblende crystals more room is also at disposal to the nearest-neighbors bond for expanding under the influence of the stretching effect.

The availability of accurate lattice dynamics calculations, including eigenvectors of the dynamical matrix and anharmonicity effects is necessary for a sound interpretation of experimental data. Unfortunately the theoretical results available up to now are quite scare, due to the lack of interest in calculating eigenvectors of the dynamical matrix and the intrinsic difficulties encountered when going beyond the harmonic approximation.

The balance between the effects of stretching and tension mechanisms giving rise to the balance between positive and negative expansion depends on the frequency distribution of normal modes as well as on their eigenvectors and grüneisen parameter. The Einstein frequencies of the EXAFS MSRDs can be compared with the calculated dispersion curves and phonon density of states (DOS) of Ge [113], CdTe [90] and CuCl [88]. The calculated phonon DOS of Ge, CdTe and CuCl as shown in Fig. (5.9) are characterized by three well-separated groups of frequencies [91]: transverse acoustic (TA) modes, longitudinal acoustic (LA) modes and optical modes. For the studied crystals, the EXAFS Einstein frequencies do not correspond to definite peaks in the phonon DOS. The comparison between EXAFS MSRDs and calculated DOS, suggests anyway that the low-energy TA modes play a more determined role for perpendicular relative motion than the LA and optical modes.

The low-temperature NTE effect is particularly marked for crystals of open structure with relatively small shear moduli; actually, small shear moduli correspond to low frequencies for the transverse acoustic modes, which are the only ones excited at low temperatures. Transverse acoustic modes have been often associated with NTE in zincblende structures; ab initio calculations performed in the framework of the quasi-harmonic approximation (QHA) have shown that in CuCl the TA mode at zone boundary points (X and L) have a negative grüneisen parameter and therefore contribute to NTE. A negative grüneisen parameter for TA modes at the zone boundary was found also in diamond crystals from pressure dependence of the phonon frequencies [79, 114].



Figure 5.9. The calculated dispersion curves and phonon density of states (DOS) of Ge [113], CdTe [90] and CuCl [88].

5.4 Comparison: EXAFS - VFF model

The Valence force field (VFF) model, developed to represent the short-range interactions in tetrahedrally coordinated crystals (see sec. 3.2.1), is particularly suitable for a comparison with EXAFS results. In the VFF model all interatomic forces are resolved into bond-stretching and bond-bending forces. The force constants k_r and k_{θ} of the VFF model considered here have been obtained from the expansion of VFF energy using Keating approximation [97]. The k_r and k_{θ} have been calculated from the Keating parameters α and β as in Ref. [97]:

$$k_r = 3\alpha + \frac{1}{2}\beta \tag{5.2}$$

$$k_{\theta} = 2\beta/3 \tag{5.3}$$

The Keating parameters α and β had been deduced experimentally from the bond lengths and elastic constants [94] (see sec. 3.2.1). Let us now try to connect the short range valence force constants k_r and k_{θ} with the effective force constants obtained from EXAFS MSRDs. It is clear since the beginning that the comparison between the stretching force constants k_{\parallel} and k_r is much more justified than the comparison between the perpendicular and bending force constants k_{\perp} and k_{θ} , respectively.

Actually (Fig. 5.10), k_{θ} measures the stiffness of the angle θ between two adjacent bonds, while k_{\perp} measures the resistance against bending of a single bond. For better understanding the correlation between these force constants, the values of k_{\parallel} , k_{\perp} from EXAFS and k_r , k_{θ} from VFF model for Ge, CdTe and CuCl are anyway compared in table (5.5).

5.4.1 Bond Stretching

The bond stretching force constants k_{\parallel} and k_r from EXAFS and VFF model, respectively, are listed in table (5.5) for Ge, CdTe and CuCl and shown in Fig. (5.11) as a function of ionicity. There is a reasonable agreement between k_{\parallel} and k_r values for the different systems, as well as a good agreement in the trend as a function of the bond ionicity: both the force constants decreases in going from Ge to CdTe to CuCl. The ratio k_{\parallel}/k_r , listed in table (5.5) is about 1 for Ge and decreases with the ionicity to



Figure 5.10. Schematic illustration of the bond length and bond angles of the VFF model and EXAFS thermal relative elliposid.

Table 5.5. Comparison of parallel and perpendicular effective force constants, k_{\parallel} , k_{\perp} from EXAFS and short range forces k_r and k_{θ} of VFF-model for Ge, CdTe and CuCl crystals.

	k_\parallel	k_r	k_{\parallel}/k_r	k_{\perp}	$k_{ heta}$	k_{\perp}/k_{θ}	$k_{\parallel} \ (2^{nd} \ \text{shell})$
	$eV/(\mathring{A}^2)$	$eV/(\mathring{A}^2)$		$eV/(\mathring{A}^2)$	$eV/(\mathring{A}^2)$		$eV/({\mathring{A}}^2)$
Ge	8.05	7.6	1.06	2.89	0.47	6.1	2.18
CdTe	3.8	5.52	0.69	0.9	0.1	9	0.86
CuCl	1.4	2.39	0.6	0.26	0.04	6	0.36



Figure 5.11. Comparison of the effective bond-stretching force constant, k_{\parallel} from EXAFS and short range valence force constant k_r from VFF model of Ge, CdTe and CuCl as a function of bond ionicity.

about 0.6 for CuCl.

5.4.2 Bond Bending

The force constants k_{\perp} and k_{θ} from EXAFS and VFF model, respectively, are listed in table (5.5) and shown in Fig. (5.12) as a function of bond ionicity. As expected k_{θ} , referring to the variation of the angle between the bonds, is different from k_{\perp} , referring to the oscillations of a single bond (see Fig. 5.10). The k_{θ} values are much smaller than k_{\perp} , however one can observe that both force constants decreases with increasing the bond ionicity, and that their ratio k_{\perp}/k_{θ} (see table 5.5) is restricted between the value 6 for Ge and CuCl and 9 for CdTe.

The comparison between the anisotropy of relative atomic motion $\xi = k_{\parallel}/k_{\perp}$ and the short-range forces ratio k_r/k_{θ} for Ge, CdTe and CuCl is made in Fig. (5.13). The calculated values of anisotropy from EXAFS and from VFF model increase with increasing the bond ionicity from Ge to CuCl. According to the higher values of k_{θ} (see Fig. 5.12), the VFF anisotropy is much larger than anisotropy of relative vibration from EXAFS. The ratio between the anisotropy parameters of EXAFS and VFF is about 6 for Ge, 13 for CdTe and 11 for CuCl.



Figure 5.12. Comparison of the force constants, k_{\perp} from EXAFS and k_{θ} from VFF-model of Ge, CdTe and CuCl as a function of bond ionicity.



Figure 5.13. Comparison between k_{\parallel}/k_{\perp} from EXAFS and k_r/k_{θ} from VFF-model of Ge, CdTe and CuCl as a function of bond ionicity.



Figure 5.14. Comparison between effective bond-stretching force constants, k_{\parallel} of the available EXAFS (Ge-Ge, Cd-Cd and Cu-Cu) and k_{θ} of VFF-model for Ge, CdTe and CuCl as a function of bond ionicity.

It seems reasonable to compare the bending force constant of the VFF model, k_{θ} with the effective bond stretching force constant k_{\parallel} of the EXAFS second shell (see Fig. 5.10). The available data allow us to perform a correct comparison only for germanium. Actually we have no data on the (Te-Te) pairs in CdTe and (Cl-Cl) pairs in CuCl. We decided anyway to use the available data of the pairs (Cd-Cd) and (Cu-Cu) in CdTe and CuCl, respectively. The substitution of Cd for Te can be justified by the small difference of masse between Cd and Te, while the substitution of Cu for Cl appears more problematic due to the large difference in their atomic masses.

The available data of k_{\parallel} of EXAFS 2^{nd} shell of Ge-Ge, Cd-Cd and Cu-Cu are about 2.18, 0.86 and 0.36 $eV/(\text{\AA}^2)$, respectively and are compared with k_{θ} in Fig. (5.14). There is still a non-negligible difference and the ratio between k_{\parallel}/k_{θ} is about 4.6 for Ge, 8.49 for CdTe and 8.64 for CuCl.

5.4.3 General comments

The difficulty in evaluating the error bars particularly for k_{\perp} of EXAFS and k_r , k_{θ} of VFF model limits the quantitative reliability of the comparison between EXAFS and

VFF force constants. Besides, one should always consider the basic difference between the effective EXAFS pair potentials and the *bare* interaction potentials. In principle, the effective EXASF pair potential depends on the statistically averaged behavior of all atoms in the crystal.

Recently, by taking into account only the nearest-neighbors interactions in copper and Nickel, it has been shown that the effective stretching pair potential is significantly stronger and less asymmetric than single-bond potential [115]. However, Zincblende crystals with open structure (low coordination number) can offer more free room for the nearest neighbors bond to expand or contract under the influence of the stretching or bending effects, respectively. This Fact could qualitatively explain the agreement between k_r and first shell k_{\parallel} .

The stretching and bending force constants from EXAFS and VFF model are different and this can be related to the difference between *effective pair* potential and *bare* interaction potential. Therefore, EXAFS can give unique insight on the interpretation of the local origin of NTE within the phenomenological models of NTE based on the competition between stretching and tension effects.

Conclusions

EXAFS is a very appealing tool for studying the local origin of NTE, thanks to the possibility of directly and accurately measuring the true expansion of selected interatomic bonds as well as the perpendicular MSRD and the anisotropy of relative vibrations. EXAFS gives original information complementary to Bragg diffraction on the local mechanisms responsible for NTE.

In order to better understand the local origin of NTE in diamond-zincblende structure, EXAFS spectra at the K-edge of Cd in CdTe have been studied as a function of temperature, from 19 to 300K. The main results of the quantitative EXAFS analysis of CdTe are:

- Thermal expansion measured by EXAFS at all measured temperatures is positive and larger than the expansion measured by Bragg diffraction, due to the effect of perpendicular MSRD.
- The effective bond stretching and bending force constants have been calculated from the best fitting Einstein frequencies to the parallel and perpendicular MSRDs, respectively. The anisotropy of the relative vibrations calculated from the ratio of perpendicular to parallel MSRDs.
- The absolute values of third cumulant have been determined by fitting experimental data to a one-dimensional quantum perturbative model. The thermal expansion due solely to the asymmetry of the effective pair potential has been evaluated and is in disagree with both the EXAFS and crystallographic thermal expansions. This failure evidences the inadequacy of one-dimensional models for

interpreting EXAFS results in the case of a three-dimensional crystals.

- The relative vibrations parallel to the bond are strongly correlated for the first shell (Cd-Te), less for the second shell (Cd-Cd) and still less for the third shell (Cd-Te).
- The average thermal expansion of the second and third shell is positive and increases with temperature.

A critical comparison between the present results for CdTe and the results previously obtained for Ge and CuCl has been performed and can be summarized as follow:

- The expansion δC_1^* of the average distance measured by EXAFS, say the true nearest neighbor bond expansion is always positive and increases with increasing the bond ionicity.
- The thermal expansion δC_1^* measured by EXAFS is larger than the crystallographic expansion δR_c , the difference increases from Ge to CuCl due to the effect of perpendicular MSRD; the stronger is the negative crystallographic expansion, the larger is the positive EXAFS expansion.
- The bond thermal expansion, δC_1^* is a joint effect of asymmetry (third cumulant) and shift of the effective potential. A relevant contribution to the potential shift is related to vibrations perpendicular to the bond.
- The increase of the bond ionicity in going from Ge to CdTe to CuCl, accompanied by the increase of the bond PTE and by the increase of the lattice NTE strength can be correlated to the following observations:
 - A reduction k_{\parallel} , corresponding to a looser bond. The bond PTE measured by EXAFS is connected to the bond stretching effect.
 - The large difference $\delta C_1^* \delta R_c$, due to the increasing influence of the transverse acoustic modes with a negative Grünesein parameter, reflects on the perpendicular MSRD and is measured by the reduction of k_{\perp} . The perpendicular MSRD can be connected to the tension effect.

- EXAFS PTE, which directly reflects the effect of bond stretching, is also connected with the positive shift of the minimum of the effective potential, which in turn is connected to the perpendicular MSRDs.
- Increasing the anisotropy ratio k_{\perp}/k_{\parallel} . The strength of NTE is correlated to anisotropy of relative atomic vibrations.
- The asymmetry of the distribution of distances β increases.
- The difference between force constants of the effective EXAFS pair potentials and single bare pair potentials of VFF model seems limited only to the bending forces. The similarity for the stretching forces could be related to the relatively open structure of the zincblende crystals.

Bibliography

- [1] J. S. O. Evans. J. Chem. Soc. Dalton Trans., 19:3317, 1999.
- [2] K. Rottger, A. Endriss, J. Ihringer, S. Doyle, and W. F. Kuhs. Acta Cryst., Sect. B, 50:644, 1994.
- [3] G. K. White. Contemp. Phys., 34:193, 1993.
- [4] V. Heine, P. R. L. Welche, and M. T. Dove. J. Am. Ceram. Soc., 82:1793, 1999.
- [5] J. N. Grima, V. Zammit, and R. Gatt. Xjenza, 11:17, 2006.
- [6] G. D. Barrera, J. A. Bruno, T. H. K. Barron, and N. L. Allan. J. Phys. Condens Matter, 17:217, 2005.
- [7] T. A. Mary, J. S. O. Evans, T. Vogt, and A. W. Sleight. Science, 272:90, 1996.
- [8] J. Tao and A. Sleight. J. Solid State Chem., 173:442, 2003.
- [9] G. Bunker. Nucl. Instrum. Methods, 207:437, 1983.
- [10] P. Fornasini, F. Monti, and A. Sanson. J. Synchrotron Rad., 8:1214, 2001.
- [11] S. a Beccara, G. Dalba, P. Fornasini, R. Grisenti, and A. Sanson. Phys. Rev. Lett., 89:25503, 2002.
- [12] P. Fornasini, S. I. Ahmed, A. Sanson, and M. Vaccari. Phys. Status Solidi B, 245:2497, 2008.
- [13] P. Fornasini, N. Abd el All, S. I. Ahmed, A. Sanson, and M. Vaccari. Journal of Physics : Conference Series, 190:012025, 2009.

- [14] S. a Beccara. Path Integral Monte Carlo Calculation of EXAFS Cumulants. PhD thesis, PhD thesis, Universita' degli studi di Trento, 2003.
- [15] R. Roy, D. K. Agrawal, and H. A. McKinstry. Annu. Rev. Mater. Sci., 19:59, 1989.
- [16] N. W. Ashcroft and N. D. Mermin. Solid State Physics. Saunders College; Tokyo: CBS PUBLISHING JAPAN, LTD, 1976.
- [17] T. H. K. Barron, J. G. Collins, and G. K. White. Adv. phys., 29:609, 1980.
- [18] T. H. K. Barron, J.A. Birch, and G. K. White. J. Phys. C: Solid State Phys., 10:1617, 1977.
- [19] A. Sanson, G. Dalba, P. Fornasini, R. Grisenti, F. Rocca, G. Artioli, M. Dapiaggi, and W.Tiano. *Physica Scripta*, T115:143, 2005.
- [20] W. Tiano, M. Dapiaggi, and G. Artioli. J. Appl. Cryst., 36:1461, 2003.
- [21] P. Fornasini, A. Sanson, M. Vaccari, G. Artioli, and M. Dapiaggi. Journal of Physics : Conference Series, 92:012153, 2007.
- [22] A. Sanson, F. Rocca, G. Dalba, P. Fornasini, R. Grisenti, M. Dapiaggi, and G. Artioli. *Phys. Rev. B*, 73:214305, 2006.
- [23] K. W. Chapman, P. J. Chupas, and C. J. Kepert. J. Am. Chem. Soc., 127:15630, 2005.
- [24] P.Fornasini, S. a Beccara, G. Dalba, R. Grisenti, A.Sanson, M.Vaccari, and F. Rocca. *Phys. Rev. B*, 70:174301, 2004.
- [25] M. G. Tucker, M. T. Dove, and D. A. Keen. J. Phys. Condens Matter, 12:L723, 2000.
- [26] T. H. K. Barron. Phil. Mag., 46:720, 1955.
- [27] M. Blackman. Phil. Mag., 3:831, 1958.
- [28] M. T. Dove. Introduction to lattice dynamics. Cambridge university press, 1993.

- [29] E. A. Stern, P. Livins, and Z. Zhang. *Phys. Rev. B*, 43:8850, 1991.
- [30] J. C. Phillips. Rev. Mod. Phys., 42:317, 1970.
- [31] J. C. Phillips and J. A. Van Vechten. Phys. Rev. B., 2:2147, 1970.
- [32] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho. Phys. Rev. B, 43:5024, 1991.
- [33] G. Dolling and R. A. Cowley. Proc. Phys. Soc., 88:463, 1966.
- [34] S. I. Ahmed, G. Dalba, P. Fornasini, M. Vaccari, F. Rocca, A. Sanson, J. Li, and A. W. Sleight. *Phys. Rev. B*, 79:104302, 2009.
- [35] G. Dalba, P.Fornasini, R. Gotter, and F. Rocca. Phys. Rev. B, 52:149, 1995.
- [36] G. Dalba, P.Fornasini, R. Grisenti, and J.Purans. Phys. Rev. Lett., 82:4240, 1999.
- [37] S. a Beccara and P. Fornasini. Phys. Rev. B, 77:172304, 2008.
- [38] M. Vaccari, R. Grisenti, P. Fornasini, F. Rocca, and A. Sanson. Phys. Rev. B, 75:184307, 2007.
- [39] E. Weihreter. Compact sycnchrotron light sources. World Scientific, 1996.
- [40] D. E. Sayers, E. A. Stern, and F. W. Lytle. Phys. Rev. Lett., 27:1204, 1971.
- [41] M. Newville, 2003. urlhttp://faculty.mc.yu.edu/afrenkel/workshops-courses.htm.
- [42] M. Newville, 2006. urlhttp://faculty.mc.yu.edu/afrenkel/workshops-courses.htm.
- [43] B. K. Agarwal. X-ray Spectroscopy: An Introduction. Springer-Verlag; 2-nd edition, 1991.
- [44] D. C. Konigsberger and R. Prins. X-ray absorption: principles and application techniques. J. Wiley, New York, 1988.
- [45] J. Sthr. NEXAFS Spectroscopy. Springer, Berlin, 1996.

- [46] P. Fornasini. Synchrotron Radiation: Fundamentals, Methodology, and Applications. Editted by S. Mobilio and G. Vlaic. SOCIETÀ ITALIANA DI FISICA, Conf. Proc. 82, 2001.
- [47] P. A. Lee and J. B. Pendry. *Phys. Rev. B*, 11:2795, 1975.
- [48] B. K. Teo. EXAFS: Basic Principle and Data analysis. Springer, New Yourk, 1986.
- [49] S. J. Gurman and R. F. Pettifer. *Phil. Mag. B*, 40:345, 1979.
- [50] J.Mustre de Leon J.Rehr, S.Zabinsky, and R.Albers. Am. Chem. Soc., 113:5135, 1991.
- [51] M. Weissbluth. photon-Atomic Interaction. Academic Press, Inc., 1989.
- [52] S. Zabinsky J. Rehr and R. Albers. Phys. Rev. Lett., 69:3397, 1992.
- [53] A. Filipponi. J.Phys. Condense. Matter, 13:23, 2001.
- [54] R. Kubo. Phys. Soc. Japan, 17:975, 1962.
- [55] J. Freund, R. Ingalls, and E. D. Crozier. *Phys. Rev. B*, 39:12537, 1989.
- [56] M. Vaccari. Local Dynamics and Negative Thermal Expansion: an EXAFS Study of CuCl. PhD thesis, Universita' degli studi di Trento, 2006.
- [57] P. Fornasini. J. Phys. Condens Matter, 13:7859, 2001.
- [58] W. R. Busing and H. A. Levy. Acta Cryst., 17:142, 1964.
- [59] G. Beni and P. M. Platzman. Phys. Rev. B, 14:1514, 1976.
- [60] A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova. Theory of lattice dynamics in the harmonic approximation. Academic Press Inc. New York, 1971.
- [61] G. Dalba and P. Fornasini. J. Synchrotron Rad., 4:243, 1997.

- [62] M. Dapiaggi, W. Tiano, G. Artioli, A. Sanson, and P. Fornasini. Nucl. Instr. Methods, 200:231, 2003.
- [63] B. T. M. Willis and A. W. Pryor. Thermal Vibrations in Crystallography. Cambridge University Press, 1975.
- [64] T. Ishii. J. Phys. Condens Matter, 4:8029, 1992.
- [65] M. Vaccari and P. Fornasini. J. Synchrotron Radiat., 13:321, 2006.
- [66] E. Sevillano, H. Meuth, and J. J. Rehr. Phys. Rev. B, 20:4908, 1979.
- [67] A. I. Frenkel and J. J. Rehr. Phys. Rev. B, 48:585, 1993.
- [68] N. V. Hung and J. J. Rehr. J. Phys. Rev. B, 56:43, 1997.
- [69] A. Sanson. J. Synchrotron Rad., 15:427, 2008.
- [70] L. Troger, T. Yokoyama, D. Arvanitis, T. Lederer, M. Tischer, and K. Baberschke. *Phys. Rev. B*, 49:888, 1994.
- [71] G. Dalba, P. Fornasini, R. Grisenti, D. Pasqualini, D. Diop, and F. Monti. Phys. Rev. B, 58:4793, 1998.
- [72] T. Yokoyama. J. Synchrotron Rad., 6:121, 1999.
- [73] M. Vaccari and P. Fornasini. *Phys. Rev. B*, 72:092301, 2005.
- [74] J. Munstre de leon, S.D. Conradson, I. Batistic, A. R. Bishop, I. D. Raistrick,
 M. C. Aronson, and F. H. Garzon. J. Phys. Rev. B, 45:2447, 1992.
- [75] J. M. Tranquada and R. Ingalls. Phys. Rev. B, 28:3520, 1983.
- [76] A. B. Edwards, D. J. Tildesley, and N. Binsted. Mol. phys., 91:357, 1997.
- [77] M. Newville and E. A. Stern. urlhttp:// krazy. phys. washington. edu/paper/agau.html.
- [78] T. Miyanaga and T. Fujikawa. J. Phys. Soc. Japan, 63:1036, 1994.

- [79] R. T. Payne. Phys. Rev. Lett., 13:53, 1964.
- [80] M. Blackman. Proc. Phys. Soc. B, 70:827, 1957.
- [81] T. H. K. Barron. Ann. Phys., 1:77, 1957.
- [82] W. Weber. Phys. Rev. Lett., 33:371, 1974.
- [83] H. Wendel and R. M. Martin. *Phys. Rev. B*, 19:5251, 1979.
- [84] M. T. Yin and M. L. Cohen. Phys. Rev. B, 26:3259, 1982.
- [85] W. B. Daniels. Phys. Rev. Lett., 8:3, 1962.
- [86] R. D. Mccammon and G. K. White. Phys. Rev. lett., 10:234, 1963.
- [87] A. Bienenstock. Phil. Mag., 9:755, 1964.
- [88] Y. Ma, J. S. Tse, and D. D. Klug. Phys. Rev. B, 67:140301, 2003.
- [89] M. B. Kanoun, W. Sekkal, H. Aourag, and G. Merad. Phy. Lett. A, 272:113, 2000.
- [90] E. Deligoz, K. Colakoglu, and Ciftci. *Physica B*, 373:124, 2006.
- [91] B. D. Rajput and D. A. Browne. *Phys. Rev. B*, 53:9052, 1996.
- [92] J. M. Rowe, R. M. Nicklow, D. L. Price, and K. Zanio. *Physica B*, 10:671, 1974.
- [93] D. N. Talwar and K. Holliday. *Physica B*, 263:540, 1999.
- [94] R. M. Martin. Phys. Rev. B, 1:4005, 1970.
- [95] Y. Yn Peter and Manuel Cardona. Fundamentals of Semiconductor. Springer Berlin Heidelberg New York, 2005.
- [96] M. J. P. Musgrave and J. A. Pople. Proc. Roy. Soc. (London), A268:474, 1962.
- [97] P. N. Keating. *Phys. Rev*, 145:637, 1966.
- [98] L. Kleinman. Phys. Rev., 128:2614, 1962.

- [99] A. Bienenstock and G. Burley. Phys. Chem. Solids, 24:1271, 1963.
- [100] T. H. K. Barron and G. K. White. Kluwer Academic/ Plenum Publishers, New York, 1999.
- [101] A. Filipponi, M. Borowski, D.T. Bowron, S.Ansell, S. De Panfilis, A. Di Cicco, and J.P. Itie. *Phys.Rev. Sci. Instruments*, 71:2422, 2000.
- [102] P. Fornasini. Ternto university, italy, 2007.
- [103] R.W.G. Wyckoff. Crystal Structures, Vol. 1. John Wiley and Sons, New York, London, 1963.
- [104] B. Ravel and M. Newville. J. Synchrotron Rad., 12:537, 2005.
- [105] J. Mustre de Leon, J.Rehr, S.Zabinsky, and R. Albers. Phys. Rev. B, 44:4146, 1991.
- [106] E. A. Stern. Phys. Rev. B, 48:9825, 1993.
- [107] R. D. Horning and J. L. Staudenmann. Phys. Rev. B, 34:3970, 1986.
- [108] P. Fornasini, G. Dalba, R. Grisenti, J. Purans, M. Vaccari, F. Rocca, and A. Sanson. Nucl. Instrum. Methods Phys. Res. B, 246:180, 2006.
- [109] G. Dalba, P.Fornasini, R. Grisenti, and J. Purans. Phys. Rev. Lett, 21:4240, 1995.
- [110] T. Ishii. J. Phys. Soc. Jpn., 70:159, 2001.
- [111] G. Dalba, P.Fornasini, M. Grazioli, and F. Rocca. Phys. Rev. B, 52:15, 1995.
- [112] J. Li, A. W. Sleight, C. Y. Jones, and B. H. Toby. *j. Solid St. Chemistry*, 178:285, 2005.
- [113] G. Nelin and G. Nilsson. *Phys. Rev. B*, 5:3151, 1972.
- [114] B. A. Weinstein and G. J. Piermarini. Phys. Rev. B, 12:1172, 1975.
- [115] N. Van Hung and P. Fornasini. J. Phys. Soc. Jpn., 76:084601, 2007.