EXAFS Investigations of the Local Thermal Properties of Solids*

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Understanding the effects of thermal disorder on EXAFS allows one to increase the accuracy of structural parameters and gives original insights on the local dynamical properties of materials. In this paper, a synthetic account is given of the progressive development of the comprehension of thermal effects on the nearest-neighbor distance distribution, and some of the most recent achievements are highlighted. [DOI: 10.1380/ejssnt.2012.480]

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I. INTRODUCTION

A thorough understanding of the effects of thermal disorder on EXAFS is important for two orders of reasons: it allows one to increase the accuracy of the structural parameters obtained from EXAFS analysis and it gives original insights on the local dynamical properties of materials.

A progressive refinement of this understanding has been achieved since the Seventies, thanks to accurate experiments and theoretical advancements, from the pioneering interpretation of the EXAFS Debye-Waller factor in the harmonic approximation [1] to the introduction of anharmonic contributions [2, 3] via the cumulant expansion method [4–6] to the development of quantum statistical approaches [7, 8].

Particularly significant are the results obtained for the nearest-neighbors (first-shell) coordination, where the data analysis can be performed within the single scattering approximation by two alternative procedures (ratio method and non-linear fitting of theory to experiment), and the accuracy of results can be more easily checked against theoretical calculations [9–11].

The possibility of directly measuring the bond thermal expansion and, by comparison with the lattice thermal expansion, the perpendicular mean square relative displacement has been recently demonstrated, giving original insights on the local origin of negative thermal expansion in crystals [12–14] and opening new perspectives for the interpretation of EXAFS data on more complex systems, such as nano-particles, surfaces and interfaces.

In this paper, a synthetic account is given of the progressive development of the comprehension of thermal effects on the nearest-neighbor distance distribution, and some of the most recent achievements are highlighted.

II. ONE-DIMENSIONAL MODEL

The information obtainable from EXAFS for an isotropic sample is one-dimensional.

Let us consider the first-shell contribution to EXAFS in a crystalline system and assume for simplicity that there is no structural disorder. Owing to vibrational disorder (zero-point energy plus thermal motion), the EXAFS signal is a configurational average over a product of distance-dependent factors [15, 16]:

\[
\chi(k) \propto \left\{ \exp\left[-\frac{2r}{\lambda(k)}\right] \exp(2ikr) \right\},
\]

where \( r \) is the interatomic instantaneous distance and \( \lambda \) the electron mean free path.

Equivalently, the EXAFS signal is generally expressed in terms of the integral over a probability distribution [5, 17]

\[
\chi(k) = \frac{S^2}{k} \text{Im} \left[ f(k, \pi) e^{2ik\lambda} \int_0^\infty P(r, \lambda) e^{2ikr} \, dr \right],
\]

where \( P(r, \lambda) = \rho(r) \exp(-2r/\lambda)/r^2 \) is an effective distribution and \( \rho(r) \) is the real distribution of distances.

A. The cumulant method

For moderate degrees of disorder, the effective distribution can be expanded in a power series [4, 5]

\[
\ln \int_0^\infty P(r, \lambda) e^{2ikr} \, dr = \sum_{n=0}^{\infty} \frac{(2ik)^n}{n!} C_n,
\]

where \( C_n \) are the cumulants of the effective distribution, and the EXAFS signal can be parametrized as

\[
k\chi(k) = S_0^2 |f(k, \pi)| N \times \exp \left[ C_0 - 2k^2C_2 + (2/3)k^4C_4 + \cdots \right] \times \sin \left[ kC_1 - (4/3)k^3C_3 + \cdots \right]
\]

The first and second cumulants, \( C_1 = \langle r \rangle \) and \( C_2 = \sigma^2 = \langle (r - \langle r \rangle)^2 \rangle \), respectively, are the average value and the variance of the effective distribution. Higher order cumulants quantify the deviation of the distribution from the gaussian shape. In particular, the third cumulant \( C_3 = \langle (r - \langle r \rangle)^3 \rangle \) is a measure of the distribution asymmetry.

Neglecting the cumulants of order higher than two amounts to assuming a gaussian shape for the effective distribution of distances. This choice (the so called standard EXAFS formula) can lead to significant errors in the determination of the first-shell average distance and of the corresponding thermal expansion.

Strengths and limitations of the cumulant method have been studied by various authors [5, 18] and its inadequacy

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for systems affected by relatively strong structural disorder has been stressed [19]. For weak thermal disorder, the temperature dependence of the lowest order cumulants is expected to follow well defined analytical expressions (see below) [7, 20].

In a typical procedure of EXAFS analysis, a limited number of polynomial coefficients $C_n$ is determined (frequently $n \leq 3$). The agreement of the temperature dependence of the polynomial coefficients $C_n$ with theoretical expectations is a self-consistent check of the convergence properties of the cumulants series, so that polynomial coefficients can be considered as good estimates of the cumulants $C_n$ [6, 9, 10].

Different analytical and numerical procedures have been proposed for connecting the cumulants of the real and effective distributions ($C_n^\ast$ and $C_n$, respectively), limited to the first cumulant [4, 21] or extended to higher order cumulants [22]. A simple recursion formula is [23]

$$C_n^\ast \sim C_n + 2C_{n+1}(1/C_1 + 1/\lambda) \quad \text{for} \quad n = 1, 2, 3, \ldots$$

In most cases, the difference between the cumulants of the real and effective distributions has been found significant only for the first cumulant.

B. Cumulants and potential energy

From quantum statistical considerations, a one-dimensional distribution of distances $\rho(r)$ can be expressed as

$$\rho(r) = \frac{1}{\sqrt{2\pi}k_0} \exp(-\beta E_n) \sum_n |\phi_n(r)|^2 \exp(-\beta E_n),$$

where $E_n$ and $\phi_n(r)$ are the energy eigenvalues and eigenfunctions, respectively.

In the classical approximation, the distribution $\rho(r)$ is connected to the potential energy $V(r)$ by

$$\rho(r) = \frac{\exp[-\beta V(r)]}{\int \exp[-\beta V(r)] dr}.$$

Let us expand the potential energy as

$$V(r) = \frac{1}{2}k_0u^2 + k_3u^3 + k_4u^4 + \cdots$$

where $u = r - r_0$ is the deviation of the interatomic distance from its equilibrium value, and search for the connection between the EXAFS cumulants and the force constants $k_n$.

1. Classical approximation

For a classical oscillator, the cumulants $C_n^\ast$ of the real distribution can be expressed as [15, 24, 25]:

$$\delta C_1^\ast(T) = -\frac{3k_3}{k_0}kT + \cdots$$

$$C_2^\ast(T) = kT^2 + \frac{3}{k_0^3} \left( \frac{12k_3^2}{k_0^3} - 4k_4 \right) (kT)^2 + \cdots$$

$$C_3^\ast(T) = -\frac{6k_3}{k_0} (kT)^2 + \cdots$$

$$C_4^\ast(T) = \frac{12}{k_0^3} \left( \frac{9k_3^2}{k_0^3} - 2k_4 \right) (k_BT)^3 + \cdots$$

where $\delta C_1^\ast$ is the thermal expansion $\langle r \rangle - r_0$.

a. Harmonic approximation. In the harmonic approximation ($k_n = 0$ for $n \geq 3$) there is no thermal expansion. The second cumulant linearly depends on temperature; this behaviour is at odds with experimental results at low temperatures, where quantum effects are non negligible. Higher order cumulants are zero.

b. Anharmonicity effects. The main effect of anharmonicity is thermal expansion. In the classical approximation, to first order $\delta C_1^\ast = C_3^\ast/2C_2^\ast$; this simple relation is not reproduced by experimental results [9, 10]. Weak anharmonicity contributions affect the second cumulant [26]. The $T^2$ first-order dependence of the third cumulant is a good approximation of experimental values at relatively high temperatures; it neglects the weak low-temperature quantum effects [9, 10].

2. Quantum perturbative treatment

A quantitative relation between EXAFS cumulants and force constants, based on the perturbative approach of Ref. [27], has been proposed by Frenkel and Rehr [7] and extended by Yokoyama [20].

Considering the harmonic approximation as the unperturbed hamiltonian, and defining $\omega = \sqrt{k_0/\mu}$, $\sigma_0^2 = \hbar/2\mu\omega$ and $z = \exp(-\beta\omega)$, where $\mu$ is the reduced mass, one finds to first order

$$\delta C_1^\ast(T) = -\frac{3k_3\sigma_0^2}{k_0} \frac{1 + z}{1 - z} + \cdots$$

$$C_2^\ast(T) = \sigma_0^2 \frac{1 + z}{1 - z} + \cdots$$

$$C_3^\ast(T) = \left( \frac{2k_3\sigma_0^4}{k_0} \right) \frac{z^2 + 10z + 1}{(1 - z)^2} + \cdots$$

a. Harmonic approximation. In the harmonic approximation ($k_n = 0$ for $n \geq 3$), again there is no thermal expansion. The second cumulant depends on temperature according to an Einstein-like behaviour, in good agreement with experiment. Higher order cumulants are zero.

b. Anharmonicity effects. By comparing Eq. (13) with Eq. (14) one can see [7] that, to first order, the ratio

$$a = -\frac{(3k_3/k_0)}{C_2}$$

corresponds to the thermal expansion $\delta C_1^\ast$. The low-temperature quantum effects on the third cumulant are included in Eq. (15).

C. Two-atomic molecules

In the case of two-atomic molecular gases, the connection between EXAFS cumulants and force constants synthesized in Eqs. (13)-(15) is obvious. The force constants refer to the power expansion of the true potential energy, and the thermal expansion is only due to the asymmetry of the potential energy: with reference to Eq. (16), $a = \delta C_1^\ast$.

The second cumulant can be interpreted in terms of the mean square relative displacement (MSRD) of the two atoms forming the molecule.
A cumulant study of the bromine molecule Br2 has been performed by Yokoyama et al. [28].

III. MANY-ATOMIC SYSTEMS

For many-atomic molecules and condensed systems, the interpretation of EXAFS cumulants is less immediate than for two-atomic molecules. The problem here arises from the relation between the three-dimensional structure of the N-atomic system and the one-dimensional distribution $\rho(r)$ sampled by EXAFS.

For concreteness, let us consider here only the case of perfect crystals, for which the comparison between EXAFS and Bragg diffraction is particularly fruitful. The potential energy associated with the distribution of the $\rho(r)$ is now an effective (mean force) potential energy, to be distinguished both from the single-pair interaction potential energy and from the crystal potential energy, defined in a $3N$-dimensional configurational space.

A. Interatomic distance and MSRDs

The difference between EXAFS and Bragg diffraction can be traced back to the different nature of the underlying scattering processes and to the different sensitivity to the correlation of atomic motion.

Let $\vec{r}_a$ and $\vec{r}_b$ be the instantaneous positions of absorber and backscatterer atoms, respectively, $\vec{R} = (\vec{r}_b) - (\vec{r}_a)$ be their equilibrium positions, and $\vec{u}_a$ and $\vec{u}_b$ be the instantaneous thermal displacements from the equilibrium positions.

From Bragg diffraction one gets information on the distance $R = \langle |\vec{r}_a - \vec{r}_b| \rangle$ between the average positions of the two atoms, as well as on the anisotropic displacement parameters (ADP) $U_{ij}$. Once the ADPs are known, one can calculate the mean square displacements (MSD) of any of the two atoms parallel and perpendicular to the bond direction, $U_{||}$ and $U_{\bot}$, respectively.

From the EXAFS point of view, the instantaneous vector distance is $\vec{r} = \vec{R} + \Delta \vec{u}$ where $\Delta \vec{u} = \vec{u}_b - \vec{u}_a$ is the relative displacement, which is conveniently projected on the bond direction and on the perpendicular plane:

$$\Delta u_{||} = \vec{R} \cdot \Delta \vec{u}; \quad \Delta u^2_{\bot} = \Delta u^2 - \Delta u^2_{||}. \quad (17)$$

The first EXAFS cumulant corresponds to the average interatomic distance $\langle r \rangle = \langle |\vec{r}_a - \vec{r}_b| \rangle$, which, to first order in the harmonic approximation, is connected to the crystallographic distance $R = (\vec{r}_b) - (\vec{r}_a)$ by [9, 29-31]

$$C^*_1 = \langle r \rangle \simeq R + \langle \Delta u^2_{||} \rangle/2R. \quad (18)$$

The two distances $\langle r \rangle$ and $R$ have been recently distinguished as “real” and “apparent” bond-lengths, respectively, and their temperature dependencies as real and apparent bond expansions [32]. In principle, the direct measurement of the true bond length by EXAFS represents the solution of an old crystallographic problem, which has been for a long time faced by approximate models, such as the riding model or the TLS model [30].

The possibility of achieving, in the determination of absolute distances by EXAFS, an accuracy comparable to that of Bragg diffraction is however still problematic.

B. Parallel MSRD

One can show that the leading contribution to the second cumulant (Debye-Waller exponent $\sigma^2$) is the parallel MSRD [1]

$$\langle \Delta u^2_{||} \rangle = \langle [\hat{R} \cdot (\vec{u}_b - \vec{u}_a)]^2 \rangle$$

$$= \langle (\hat{R} \cdot \vec{u}_b)^2 \rangle + \langle (\hat{R} \cdot \vec{u}_a)^2 \rangle - 2 \langle \hat{R} \cdot \vec{u}_b \rangle \langle \hat{R} \cdot \vec{u}_a \rangle. \quad (19)$$

The first two terms are the independent Mean Square Displacements (MSD) of absorber and backscatterer atoms. The third term, the Displacement Correlation Function (DCF), depends on the correlation of atomic motions.

A dimensionless correlation parameter can be defined as [33, 34]

$$\phi = \frac{\langle (\hat{R} \cdot \vec{u}_b)^2 \rangle + \langle (\hat{R} \cdot \vec{u}_a)^2 \rangle - \langle \Delta u^2_{||} \rangle}{2\sqrt{\langle (\hat{R} \cdot \vec{u}_b)^2 \rangle \langle (\hat{R} \cdot \vec{u}_a)^2 \rangle}} \quad (20)$$

c. Harmonic approximation. Within the harmonic approximation, the parallel MSRD can be connected to the eigenvalues $\omega(q, s)$ and eigenvectors $\vec{w}(q, s)$ of the dynamical matrix as

$$\langle \Delta u^2_{||} \rangle = \frac{1}{N} \sum_{q,s} \langle |Q(q, s)|^2 \rangle$$

$$\left| \frac{\vec{w}_0(q, s)e^{i\vec{q} \cdot \vec{R}}}{\sqrt{m_b}} - \frac{\vec{w}_0(q, s)}{\sqrt{m_a}} \right|^2. \quad (21)$$

where $s$ is the branch index, $N$ is here the number of primitive cells and $Q(q, s)$ is the normal coordinate of mode $(q, s)$, which contains the dependence on temperature.

The parallel MSRD peculiarly depends on the phase relations between eigenvectors, on their projections on the bond direction $\hat{R}$ and on the inter-cell phase relation $e^{i\vec{q} \cdot \vec{R}}$. Its reproduction represents a good check of lattice dynamical calculations.

d. Correlated Debye model. For monatomic Bravais crystals, the parallel MSRD can be described by an approximate correlated Debye Model [1, 35, 36]

$$\sigma^2_D = \frac{3h}{\omega^3 m} \int_0^{\infty} dw \omega \coth \frac{h \omega}{2kT} \left[ 1 - \sin(qR) \right]. \quad (22)$$

For copper, the Debye temperatures of the first, third and fourth shells are very similar (322 to 329 K) [10]. The second shell has instead a significantly lower Debye temperature (291 K), in agreement with the reduced correlation calculated for a number of fcc crystals [34]. The EXAFS Debye temperatures of copper are in good agreement with the Debye temperatures of specific heat and of x-ray diffraction.

For crystals with more than one atom per primitive cell, such as Ge, the Debye model is still able to fit the MSRD temperature dependence, but different Debye temperatures are found for different coordination shells.
e. Correlated Einstein model. A simpler alternative model, the correlated Einstein model, is often used to parametrize the temperature dependence of the parallel MSRD [36]:

\[
\sigma_E^2 = \frac{\hbar}{2\mu \omega_E} \coth \left( \frac{\hbar \omega_E}{2kT} \right) 
\]

where \( \mu \) is the reduced mass of the absorber–backscatterer atomic pair. The MSRD of different coordination shells are fit by different Einstein frequencies.

Equation (23) corresponds to the first term (harmonic) of Eq. (14). The interpretation of the one-dimensional Einstein model for many-atomic systems requires some caution. To the Einstein frequency \( \omega_E \) an effective force constant can be associated, \( k_\parallel = \mu (\omega_E)^2 \). The force constant \( k_\parallel \) refers to an effective (mean-field) pair potential that depends on the statistically averaged influence of all the other atoms and cannot, in principle, be identified with the force constant of a single-bond potential [42].

C. Anharmonic effective potential

The relationship between the EXAFS cumulants and the effective potential on the one hand, and the 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 [17, 19] and its possible dependence on temperature [37, 38].

A method for calculating the EXAFS cumulants from the force constants of the crystal potential, based on first principles finite temperature many-body perturbation theory, has been proposed by Fujikawa and Miyangama [8]. The method has been thoroughly applied mainly to one-dimensional systems [39], and some attempts have been done also for fcc crystals [40].

By a simpler phenomenological approach, Hung and Rehr [41] derived an anharmonic correlated model for the effective potential taking into account the interaction of absorber and back-scatterer atoms with their nearest neighbor via a Morse potential. Calculations for Cu and Ni [42] demonstrated that the effective pair potential is significantly stronger and less asymmetric than the single-bond potential, and much better reproduces the experimental EXAFS cumulants. The comparison with experimental data revealed a good agreement for the second cumulant but non-negligible discrepancies for the first and third cumulants, which were tentatively attributed to the central nature of the Morse potential, which neglects many-body effects.

Promising results on three-dimensional systems have been obtained by path-integral techniques, based on the use of effective potentials [43] or on Monte Carlo sampling [44, 45].

D. Bond thermal expansion

According to Eq. (18), the nearest-neighbour distance measured by EXAFS is larger than the distance obtained by the refinement of Bragg diffraction patterns. Since the perpendicular MSRD \( \langle \Delta u_\perp^2 \rangle \) increases with temperature, the thermal expansion measured by EXAFS is larger than the thermal expansion measured by Bragg diffraction. The difference, of the order of some tenth of picometer at room temperature, has been experimentally detected for germanium [9] and copper [10] and reproduced by path-integral Monte Carlo simulations on copper [44].

Bragg diffraction is currently used to measure the coefficient of lattice thermal expansion \( \alpha = (1/a)(\partial a/\partial T)_p \). One can reasonably define a coefficient of bond thermal expansion, different for different coordination shells, which could be evaluated from accurate EXAFS measurements performed at sufficiently small temperature steps. Worth of particular attention is the connection between the inter-atomic distance expansion, measured by the first EXAFS cumulant, and the anharmonicity of the effective pair potential, measured by the third cumulant. Contrary to the case of two atomic molecules, it has been experimentally observed that in many-atomic systems the expansion of the nearest-neighbor distance is not completely accounted for by the asymmetry of the effective pair potential, as per Eq. (16) of the one-dimensional model. An additional rigid shift of the effective potential energy with temperature has to be assumed in order to reproduce the expansion measured by the first cumulant [9, 10, 14, 23].

The presence of a rigid shift of the maximum of the distance distribution, corresponding to the minimum of the potential energy, has been confirmed for Cu by path-integral Monte-Carlo simulations [11] and for Ge by Molecular Dynamics simulations [46]. In both cases, the simulations further show that the contribution of the potential asymmetry to thermal expansion is much smaller for the outer shells than for the first shell. The outer-shell distributions are to a good approximation gaussian, and the thermal expansion of their average distances is accounted for mainly by their rigid shift. In conclusion, no reliable information on thermal expansion can be obtained from the third cumulant. From a practical point of view, the reduced asymmetry of the outer-shells distributions suggests that the inclusion of the third cumulant, which is mandatory for accurate first-shell analyses, is much less important for the outer shells.

E. Perpendicular MSRD

In principle, the perpendicular MSRD could be obtained from the absolute values of the distances \( C^*_\perp = \langle r \rangle \) and \( R \), by inverting Eq. (18). In general, much more accurate experimental results are obtained for the relative values of \( C^*_\perp \) (often to within less than 0.001 Å) than for the absolute values. As a consequence, the temperature dependence of the perpendicular MSRD \( \langle \Delta u_\perp^2 \rangle \) can be obtained from the difference between the true and apparent bond expansions, \( \Delta C^*_\perp - \delta R_c \).

Absolute values of \( \langle \Delta u_\perp^2 \rangle \) can be recovered by fitting an Einstein correlated model to the relative values; note that the expression of the Einstein model for the perpendicular MSRD defined in Eq. (18) differs by a factor 2 from the expression for the parallel MSRD [47]. The perpendicular Einstein frequency can be connected to an effective force constant \( k_\perp = \mu (\omega_\perp)^2 \).
The ellipsoids of relative thermal vibrations of nearest-neighbours atoms are anisotropic, typically disc-shaped. A natural measure of the degree of anisotropy of relative vibrations is the ratio \( \gamma = \langle \Delta u^2 \rangle / \langle \Delta u^2 \rangle \), which is however temperature dependent [23]. A temperature-independent measure of anisotropy, corresponding to the asymptotic behaviour of the ratio \( \gamma \) for \( T \to \infty \), is given by the ratio of parallel to perpendicular effective force constants, \( \xi = k_{||}/k_{\bot} \) [48]. For perfectly isotropic relative vibrations, \( \xi = 1 \).

It is worth noting that the relative ellipsoids are anisotropic even for crystals where the atomic ellipsoids are spherical for symmetry reasons, such as copper and germanium.

The comparison of the relative thermal ellipsoids (from EXAFS) with the absolute atomic thermal ellipsoids (from Bragg diffraction) provides information on the correlation of lattice vibrations, both parallel and perpendicular to the bond. The perpendicular correlation is generally weaker than the parallel correlation.

IV. APPLICATIONS

A. Negative thermal expansion

A number of crystals are affected by NTE, within restricted low-temperature intervals as some tetrahedral semiconductors (Si, Ge, GaAs, CuCl, . . . ) [49] or in extended temperature intervals as some framework structures [50–52].

The potential of EXAFS for studying NTE materials has been little exploited. In an EXAFS study of the framework structure ZrW\(_6\)O\(_{18}\), Cao et al. limited their attention to the temperature dependencies of the parallel MSRDs of different atomic pairs [53].

According to a real-space phenomenological model, the lattice expansion is the 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 [32]. When tension effects prevail over bond stretching, the solids exhibit NTE.

Conventional techniques, such as dilatometry and Bragg diffraction, are sensitive only to the lattice thermal expansion, and cannot distinguish the bond stretching from the tension effects. These two effects can instead be disentangled by EXAFS, which directly measures the positive bond expansion (due to the stretching effect) and, by comparison with Bragg diffraction, the perpendicular MSRD (directly connected to the tension effect).

Several crystals with different structures and exhibiting different NTE properties have been recently investigated [9, 14, 23, 48, 54, 55]. The results, partially summarized in [56], confirm the possibility of disentangling the bond stretching and the tension effects and suggest that a correlation can be established between bond ionicity, negative thermal expansion properties and a number of quantities measured by EXAFS. The stronger is the NTE, the larger are the positive bond expansion, the relative atomic vibrations perpendicular and parallel to the bond, as well as their anisotropy.

Recently, the anomalously small thermal expansion of the Invar alloy Fe\(_{64.6}\)Ni\(_{35.4}\) has been investigated by Yokoyama and Eguchi [13]. Those Authors found that the first nearest-neighbour (NN) shells around Fe show almost no thermal expansion, while those around Ni exhibit meaningful but smaller expansion than that of fcc Ni, and confirmed the breakdown of the direct correspondence between thermal expansion and anharmonicity.

B. Isotopic effects

An original application of the sensitivity of EXAFS to thermal disorder has been the detection of isotopic effects in germanium [57].

The isotopic composition of crystals influences some of their basic properties, like density, phonon widths and electronic energy gaps [58]. As far as dynamical properties are concerned, while the force constants depend on atomic species and crystal structure, the zero-point amplitude of atomic vibrations is influenced by the nuclear masses, the lighter isotopes undergoing larger oscillations than the heavier ones. As a consequence of anharmonicity, the difference of zero-point amplitude of motion reflects on a difference of interatomic equilibrium distances and lattice parameters. These isotopic effects progressively disappear when the temperature increases.

EXAFS has been recently measured on two powdered samples of \(^{70}\)Ge and \(^{76}\)Ge as a function of temperature from 20 to 300 K [57]. An isotopic effect has been clearly evidenced in the behavior of the parallel MSRDs. As expected, the Einstein frequency \( \omega_E \) is lower for the heavier isotope, but the effective force constant \( k_{||} \) is the same for the two isotopes. The ratio of the zero-point values of the Einstein models, \( \sigma_0^2(70)/\sigma_0^2(76)=1.042 \), is in good agreement with the expected value \((76/70)^{1/2}\).

An isotopic effect has also been detected in the bond thermal expansion, thanks to a resolution better than 10 femtometers. The zero-point values of the nearest-neighbors average distance measured by EXAFS are consistent with the values of distance between average positions measured by Bragg diffraction [59].

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