Einstein and Debye models for EXAFS parallel and perpendicular mean-square relative displacements

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The correlated Einstein and Debye models for EXAFS parallel mean-square relative displacement (MSRD) are derived from the general expression in terms of eigenfrequencies and eigenvectors of the dynamical matrix, without *ad hoc* assumptions. The two models are generalized to parameterize also the EXAFS perpendicular MSRD. The physical meaning of Einstein frequencies, as well as the application of the Debye model to crystals with more than one atom per cell, are critically discussed.

Keywords: EXAFS; thermal disorder; mean-square relative displacements; Einstein model; Debye model.

1. Introduction

Extended X-ray absorption fine structure (EXAFS) is mainly known as a powerful structural probe for disordered systems. However, accurate temperature-dependent measurements also allow the possibility of extracting original information on thermal properties in crystals. The sensitivity of EXAFS to the relative atomic motion along the bond direction was recognized long ago (Beni & Platzman, 1976): the EXAFS Debye–Waller factor directly gives information on the parallel mean-square relative displacement ($\text{MSRD}_\parallel$) between absorber and back-scatterer atoms. The possibility of obtaining from EXAFS the mean-square relative displacement perpendicular to the interatomic bond ($\text{MSRD}_\perp$) was only exploited more recently (Dalba *et al.*, 1999; Fornasini, a Beccara *et al.*, 2004). Indeed, the local interatomic distance $\langle r \rangle = \langle |\mathbf{r}_2 - \mathbf{r}_1| \rangle$ probed by EXAFS is greater than the crystallographic distance between average positions $R_c = |\langle \mathbf{r}_2 - \mathbf{r}_1 \rangle|$ (Dalba *et al.*, 1995; Fornasini, Dalba *et al.*, 2004). The difference, of geometrical origin (Busing & Levy, 1964), can be utilized to measure the temperature dependence of $\text{MSRD}_\perp$.

The comparison between EXAFS MSRDs and absolute mean-square displacements (MSDs) obtained from X-ray diffraction (XRD) allows the evaluation of the correlation of atomic motions parallel and perpendicular to interatomic bonds. Besides being a test of lattice dynamical theories, this kind of information can be very effective in the study of phase transitions and negative thermal expansion.

In principle, the parallel and perpendicular MSRDs can be expressed, within the harmonic approximation, in terms of eigenfrequencies and eigenvectors of the dynamical matrix. Simple phenomenological models are, however, commonly used in many instances; for example, to evaluate absolute MSRDs values from the relative values obtained through the ratio method (Bunker, 1983), or to fast compare the thermal behaviour of different atomic pairs.

For the parallel MSRD, the correlated Debye and Einstein models were developed quite early (Beni & Platzman, 1976; Sevillano *et al.*, 1979). 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 (Ashcroft & Mermin, 1976), the correlated Debye model assumes a further spherical approximation of the square moduli of eigenvectors (Beni & Platzman, 1976; Sevillano *et al.*, 1979) and applies only to cubic crystals with one atom per primitive cell (for short, 'cubic Bravais crystals'). While the Einstein model for specific heats approximates the phonon spectrum with a single frequency ω_E (Ashcroft & Mermin, 1976), the correlated Einstein model (Sevillano *et al.*, 1979) is generally cast into the different framework of the one-dimensional model of EXAFS, where it considers the pair of absorber and back-scatterer atoms as an independent harmonic oscillator (Dalba & Fornasini, 1997) with frequency ω_E. Anharmonic corrections and improvements to the original correlated Einstein model were successively proposed (Frenkel & Rehr, 1993; Hung & Rehr, 1997).

The $\text{MSRD}_\parallel$ of a given atomic pair has also been expressed in terms of a local projected density of modes $\rho_R(\omega)$, taking into account the relations between eigenvectors (Sevillano *et al.*, 1979), and intrinsically different from the true phonon density of states $\rho(\omega)$. Attempts to relate $\rho_R(\omega)$ with $\rho(\omega)$, as well as the Einstein frequency with the moments of the phonon spectrum, were made assuming nearest-neighbours central force models (Lottici, 1987; Knapp *et al.*, 1985).

In spite of the widespread use of the Einstein and Debye correlated models, their rigorous derivation from the general expression of the parallel MSRD in terms of eigenfrequencies

and eigenvectors of the dynamical matrix is, to our knowledge, still lacking in the literature. In this paper we want to establish on firm grounds this derivation, within the framework of the harmonic approximation for crystals (Maradudin *et al.*, 1971). This treatment allows a critical reappraisal of the common phenomenological interpretations of the Einstein and Debye models, clarifying their strengths and limitations and contributing to avoid their misuses. Besides, our procedure easily leads to the peculiar extension of the two models to the case of perpendicular MSRD, whose relevance for the study of negative thermal expansion materials has been recently demonstrated (Fornasini *et al.*, 2006).

The paper is organized as follows. In §2 the general harmonic expressions of EXAFS MSRDs are introduced; §3 and §4 are dedicated to the Einstein and Debye models, respectively; §5 and §6 contain discussion and conclusions, respectively.

2. EXAFS mean-square relative displacements

The parallel and perpendicular MSRDs are defined as

$$\mathrm{MSRD}_\parallel = \langle |(\mathbf{u}_2 - \mathbf{u}_1) \cdot \hat{\mathbf{R}}_c|^2 \rangle \tag{1}$$

and

$$\mathrm{MSRD}_\perp = \langle \|(\mathbf{u}_2 - \mathbf{u}_1)\|^2 \rangle - \langle |(\mathbf{u}_2 - \mathbf{u}_1) \cdot \hat{\mathbf{R}}_c|^2 \rangle, \tag{2}$$

respectively. Here, $\mathbf{u}_1$ and $\mathbf{u}_2$ denote the instantaneous thermal displacements of absorber and back-scatterer atoms, respectively, from the equilibrium positions, $\mathbf{R}_c$ is the equilibrium distance between the two atoms, and $\hat{\mathbf{R}}_c$ is the corresponding unit vector. Within the harmonic approximation (Maradudin *et al.*, 1971), one can express the parallel and perpendicular MSRDs in terms of eigenfrequencies and eigenvectors of the dynamical matrix,

$$\mathrm{MSRD}_\parallel = (1/N) \sum_{\lambda,\mathbf{q}} \hbar/[2\omega(\lambda,\mathbf{q})] \coth[\beta\hbar\omega(\lambda,\mathbf{q})/2]$$
$$\times \left| [\mathbf{w}_2(\lambda,\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_c)/M_2^{1/2} \right.$$
$$\left. - \mathbf{w}_1(\lambda,\mathbf{q})/M_1^{1/2}] \cdot \hat{\mathbf{R}}_c \right|^2, \tag{3}$$

$$\mathrm{MSRD}_\perp = (1/N) \sum_{\lambda,\mathbf{q}} \hbar/[2\omega(\lambda,\mathbf{q})] \coth[\beta\hbar\omega(\lambda,\mathbf{q})/2]$$
$$\times \left\{ \left\| \mathbf{w}_2(\lambda,\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_c)/M_2^{1/2} - \mathbf{w}_1(\lambda,\mathbf{q})/M_1^{1/2} \right\|^2 \right.$$
$$- \left| [\mathbf{w}_2(\lambda,\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{R}_c)/M_2^{1/2} \right.$$
$$\left. \left. - \mathbf{w}_1(\lambda,\mathbf{q})/M_1^{1/2}] \cdot \hat{\mathbf{R}}_c \right|^2 \right\}. \tag{4}$$

In the case of 'Bravais crystals' (crystals with one atom per primitive cell), these equations become

$$\mathrm{MSRD}_\parallel = 1/(NM) \sum_{\lambda,\mathbf{q}} \hbar/[2\omega(\lambda,\mathbf{q})] \coth[\beta\hbar\omega(\lambda,\mathbf{q})/2]$$
$$\times |\mathbf{w}(\lambda,\mathbf{q}) \cdot \hat{\mathbf{R}}_c|^2 |\exp(i\mathbf{q} \cdot \mathbf{R}_c) - 1|^2, \tag{5}$$

$$\mathrm{MSRD}_\perp = 1/(NM) \sum_{\lambda,\mathbf{q}} \hbar/[2\omega(\lambda,\mathbf{q})] \coth[\beta\hbar\omega(\lambda,\mathbf{q})/2]$$
$$\times \left\{ \|\mathbf{w}(\lambda,\mathbf{q})\|^2 - |\mathbf{w}(\lambda,\mathbf{q}) \cdot \hat{\mathbf{R}}_c|^2 \right\} |\exp(i\mathbf{q} \cdot \mathbf{R}_c) - 1|^2. \tag{6}$$

In (3)–(6), N is the total number of primitive cells, $\omega(\lambda,\mathbf{q})$ are eigenfrequencies of the dynamical matrix labelled by the normal mode $(\lambda,\mathbf{q})$, and $\mathbf{w}_k(\lambda,\mathbf{q})$ are the three-dimensional eigenvectors referred to the k atom in the primitive cell.

It is worth remembering here that different dynamical matrices can exist, sharing the same eigenfrequencies but with different eigenvectors (Cochran, 1971). The reproduction of parallel and perpendicular MSRDs, experimentally obtained from EXAFS, represents an effective and peculiar test for the phase relationships between eigenvectors obtained from *ab initio* or model calculations.

3. Einstein model

The Einstein model, originally introduced for specific heats, consists of approximating the phonon spectrum with a single Einstein frequency ω_E (Ashcroft & Mermin, 1976),

$$\omega(\lambda,\mathbf{q}) = \omega_E \qquad \forall \quad \lambda = 1, 2, \ldots, 3r. \tag{7}$$

Equivalently, the Einstein model substitutes the phonon density of states $\rho(\omega)$ with a delta function centred at ω_E,

$$\rho^{\mathrm{ein}}(\omega) \propto \delta(\omega - \omega_E). \tag{8}$$

3.1. Parallel MSRD

Introducing the Einstein approximation of (7) into (3) and expanding the square modulus, one finds

$$\mathrm{MSRD}_\parallel = \hbar/(2N\omega_E) \coth(\beta\hbar\omega_E/2)$$
$$\times \sum_{\lambda,q} \left\{ (1/M_2)|\mathbf{w}_2 \cdot \hat{\mathbf{R}}_c|^2 + (1/M_1)|\mathbf{w}_1 \cdot \hat{\mathbf{R}}_c|^2 \right.$$
$$- [1/(M_1 M_2)^{1/2}](\mathbf{w}_2 \cdot \hat{\mathbf{R}}_c)(\mathbf{w}_1^* \cdot \hat{\mathbf{R}}_c) \exp(i\mathbf{q} \cdot \mathbf{R}_c)$$
$$\left. + \mathrm{c.c.} \right\},$$

where the $(\lambda,\mathbf{q})$-dependence of eigenvectors has been omitted for brevity. Denoting by α,β the Cartesian components of eigenvectors, making use of the closure-completeness relations (Maradudin *et al.*, 1971),

$$\sum_\lambda w_{\alpha,k}(\lambda,\mathbf{q}) w_{\beta,\nu}^*(\lambda,\mathbf{q}) = \delta_{\alpha,\beta} \delta_{k,\nu}, \tag{9}$$

and keeping in mind that $\hat{\mathbf{R}}_c$ is an unit vector, one can show that

$$\sum_\lambda \sum_{\alpha,\beta} w_{\alpha,k}(\lambda,\mathbf{q}) R_\alpha w_{\beta,\nu}^*(\lambda,\mathbf{q}) R_\beta = \delta_{k,\nu},$$

and finally obtain

$$\text{MSRD}_\parallel = \hbar/(2\mu\omega_E)\coth(\beta\hbar\omega_E/2)$$
$$\times\left\{1 - 2\mu/[N(M_1 M_2)^{1/2}]\delta_{1,2}\sum_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{R}_c)\right\},$$

where it has been taken into account that the sum over $\mathbf{q}$, extending over the first Brillouin zone, contains N values of wavevectors and is symmetric with respect to $\mathbf{q} = 0$. Besides, one has introduced the reduced mass $\mu = M_1 M_2/(M_1 + M_2)$.

Now, the term $\delta_{1,2}\sum_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{R}_c)$ is always zero. This can be understood considering two distinct cases: (i) if the two atoms 1 and 2 occupy different symmetry positions in the crystal (*i.e.* they are labelled by two different indexes within the primitive cell) then $\delta_{1,2} = 0$; (ii) if the two atoms 1 and 2 have the same symmetry positions in the crystal, then $\delta_{1,2} = 1$ but the equilibrium interatomic distance $\mathbf{R}_c$ is a non-zero vector of the Bravais lattice. In this case, $\sum_{\mathbf{q}}\exp(i\mathbf{q}\cdot\mathbf{R}_c) = 0$ (Ashcroft & Mermin, 1976). Therefore, one finally obtains

$$\text{MSRD}_\parallel^{\text{ein}} = \hbar/(2\mu\omega_E)\coth(\beta\hbar\omega_E/2). \qquad (10)$$

The Einstein approximation, (8), is in principle rather crude. It is, however, a matter of experience that the temperature dependence of the parallel MSRD is satisfactorily fitted by (10), at least within the current experimental uncertainties. This fact is not surprising, since at high temperatures equation (10) is approximated by the classical linear behaviour anyway, while at low temperatures the behaviour of the MSRD is less sensitive to the peculiarity of the model than the specific heat.

The success of (10) has been boosted by its current phenomenological interpretation (Sevillano *et al.*, 1979), which considers the pair of absorber and back-scatterer atoms as an independent Einstein oscillator with frequency ω_E related to a local effective bond-stretching force constant $\kappa = \mu\omega_E^2$ (Dalba & Fornasini, 1997). The Einstein frequency has thus a double meaning: (i) an effective vibrational frequency of the interatomic bond; (ii) a constant which roughly represents the centroid of the distribution of normal mode frequencies.

3.2. Perpendicular MSRD

The derivation in the previous paragraph can be easily extended to the case of the perpendicular mean-square relative displacement. One can proceed in an absolutely analogous way to the case of MSRD$_\parallel$: applying into (4) the Einstein approximation of (7) and the closure-completeness relation of (9), one arrives at the correlated Einstein model for the perpendicular MSRD,

$$\text{MSRD}_\perp^{\text{ein}} = \hbar/(\mu\omega_E)\coth(\beta\hbar\omega_E/2). \qquad (11)$$

The analytical expression for the perpendicular MSRD, (11), corresponds to the expression for the parallel MSRD, (10), apart from a factor 2. There is, however, no *a priori* reason why, for a given pair of atoms, the temperature dependence of the parallel and perpendicular MSRDs should be best-fitted by the same Einstein frequency.

4. Debye model

The Debye model, widely used for specific heats and diffraction MSDs, applies in principle only to monatomic 'Bravais crystals' and consists of (Ashcroft & Mermin, 1976): (i) linearly approximating the (acoustic) phonon spectrum

$$\omega(\lambda,\mathbf{q}) = v_s q \quad \forall \quad \lambda = 1, 2, 3, \qquad (12)$$

where v_s is the sound velocity in the crystal; (ii) replacing the first Brillouin zone with a sphere of radius q_D (Debye wavevector) containing the same number N of wavevectors,

$$q_D = \left(6\pi^2 N/V\right)^{1/3}, \qquad (13)$$

where V is the total volume of the crystal. The Debye model is characterized by an (acoustic) phonon density of states,

$$\rho^{\text{deb}}(\omega) \propto \omega^2/\omega_D^3. \qquad (14)$$

4.1. Parallel MSRD

Inserting the Debye approximation of (12) into (5) and properly replacing the sum over the first Brillouin zone by an integral, one obtains

$$\text{MSRD}_\parallel = V/(NM)\times 1/(2\pi)^3\int_{\text{BZ}}\hbar/(2v_s q)\coth(\beta\hbar v_s q/2)$$
$$\times\sum_\lambda\left|\mathbf{w}(\lambda,\mathbf{q})\cdot\hat{\mathbf{R}}_c\right|^2\left|\exp(i\mathbf{q}\cdot\mathbf{R}_c) - 1\right|^2\,d\mathbf{q}. \qquad (15)$$

Using the closure-completeness relations of (9) one has

$$\sum_\lambda\left|\mathbf{w}(\lambda,\mathbf{q})\cdot\hat{\mathbf{R}}_c\right|^2 = 1.$$

Using (13) and introducing spherical coordinates r, θ and φ, one has

$$\text{MSRD}_\parallel = 3/\left(2Mq_D^3\right)\int_0^{q_D}dq\ q^2\hbar/(2v_s q)\coth(\beta\hbar v_s q/2)\,F(q), \qquad (16)$$

where

$$F(q) = \int_0^\pi\sin\theta\left|\exp(iqR_c\cos\theta) - 1\right|^2\,d\theta. \qquad (17)$$

Performing the integration in (17) and re-writing the entire expression in the frequency variable, one arrives at

$$\text{MSRD}_\parallel^{\text{deb}} = 3\hbar/M\int_0^{\omega_D}d\omega\ (\omega/\omega_D^3)\coth(\beta\hbar\omega/2)$$
$$\times\left[1 - \sin(\omega R_c/v_s)/(\omega R_c/v_s)\right]. \qquad (18)$$

With respect to previous derivations of the Debye correlated model (Sevillano *et al.*, 1979), here the use of closure-completeness relations eliminates the necessity of introducing the *ad hoc* assumption of spherical approximation for the geometrical term containing the square modulus of eigenvectors.

4.2. Perpendicular MSRD

As in the case of the Einstein model, the work of the previous paragraph can be easily extended to the perpendicular MSRD. Applying into (6) the Debye approximations of (12) and (13) and the closure-completeness of eigenvectors of (9), one obtains

$$\mathrm{MSRD}_\perp^{\mathrm{deb}} = 6\hbar/M \int_0^{\omega_D} \mathrm{d}\omega \; (\omega/\omega_{\mathrm{D}}^3) \coth (\beta\hbar\omega/2)$$
$$\times \left[1 - \sin (\omega R_c/v_s)/(\omega R_c/v_s) \right]. \qquad (19)$$

Like for the Einstein model, the analytical expression for the perpendicular MSRD for the Debye model, (19), also corresponds to the expression for the parallel MSRD, (18), apart from a factor 2. Again, there is no *a priori* reason why, for a given pair of atoms, the temperature dependence of the parallel and perpendicular MSRDs should be best-fitted by the same Debye frequency (or temperature).

5. Discussion

Both parallel and perpendicular MSRDs, according to (3) and (4), are the sum of the effects of $3Nr$ oscillators of different frequencies, weighted by different geometrical factors. The Einstein and Debye models, which are characterized by only one free parameter (the frequency ω_E or ω_D, or the corresponding temperature θ_E or θ_D), are approximations based on rather restrictive assumptions. It is a matter of experience, however, that the temperature dependence of the experimental MSRDs can be reasonably fitted by both models, the difference between the two models being generally smaller than the uncertainty of experimental data or theoretical calculations.

The main current applications of the Einstein and Debye models are: (i) to calculate absolute values of parallel and perpendicular MSRDs from the relative values obtained from the phenomenological analysis based on the ratio method; (ii) to express by one parameter the parallel MSRD at different temperatures when the data analysis is based on the best fit to theoretically simulated EXAFS spectra. It is, however, interesting to inquire on the physical meaning that can be actually attributed to the Einstein and Debye frequencies.

The Debye model, in view of the more realistic density of states, appears more suitable for a physical interpretation, at least for 'Bravais crystals'. Strengths and limitations of the Debye model are enlightened by a recent EXAFS study of copper (Fornasini, a Beccara *et al.*, 2004). The Debye temperatures best-fitting the parallel MSRD of the first four coordination shells are in reasonable overall agreement with the Debye temperatures of specific heat, Bragg diffraction and thermal diffuse scattering. However, while the EXAFS Debye temperatures are very similar for first, third and fourth coordination shells, the second shell is characterized by a smaller value, corresponding to a correlation effect smaller than expected according to the Debye model, but reproducible by more refined calculations (Jeong *et al.*, 2003).

Specific heats depend only on normal mode frequencies: as a consequence, one can also still use the Debye model for 'non-Bravais' crystals, for example by properly extending the Debye sphere and considering only the three acoustic branches (Ashcroft & Mermin, 1976). The same procedure can be performed in the case of XRD Debye–Waller factors, by assuming a spherical average of the squared moduli of eigenvectors contained in the harmonic expression of the absolute mean-square displacements (Maradudin *et al.*, 1971). Also, the Debye correlated model for EXAFS parallel MSRD is often used for 'non-Bravais' crystals. The physical meaning of this approach was shown to be questionable on the basis of experimental results on germanium (Dalba & Fornasini, 1997), where the Debye temperatures best-fitting the parallel MSRDs are very different for different coordination shells and different from the known Debye temperatures of XRD and specific heats. This work clarifies that the situation for EXAFS is more complex than for specific heats and diffraction: the general harmonic expressions of MSRDs [see (3) and (4)] contain the correlation term and then the cross 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 should not be extended to 'non-Bravais crystals'.

Further insights can be gained by comparing the parallel and perpendicular MSRDs. If the dynamical properties of a crystal could be described by a unique Debye frequency (or temperature), the perpendicular MSRD would be twice the parallel MSRD [see (18) and (19)]. This follows from 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, and the Debye model implicitly assumes isotropy. However, even in the case of the first shell of copper (Fornasini, a Beccara *et al.*, 2004; Fornasini, Dalba *et al.*, 2004), one can experimentally monitor a deviation from a pure Debye behaviour: the Debye temperatures best fitting the perpendicular and parallel MSRDs are different, and the perpendicular/parallel ratio γ is non-negligibly greater than 2.

Let us now consider the Einstein model. The comparison of the Einstein frequencies, obtained from the best fit to the temperature dependence of experimental data, with the dispersion curves and the phonon density of states (DOS) is far from trivial. For both parallel and perpendicular MSRDs, ν_E is a single frequency which approximates the whole phonon spectrum. A comparison of the EXAFS Einstein frequencies (Table 1) with the phonon DOS of copper (Nilsson & Rolandson, 1973) and germanium (Nelin & Nilsson, 1972) shows that in both cases the Einstein frequencies do not correspond to any definite peak in the phonon DOS, since obviously every lattice mode contributes to the MSRDs.

Qualitative information can, however, be obtained in some cases. For germanium (Dalba *et al.*, 1999; Fornasini, Dalba *et al.*, 2004) the perpendicular to parallel anisotropy of relative atomic vibrations is much larger than for copper and the perpendicular/parallel ratio γ reaches a value of 6 at high temperatures. This fact reflects the more open crystal structure

Table 1
Einstein frequencies $\nu_E = \omega_E/2\pi$ (in THz) best fitting the parallel ($\parallel$) and perpendicular ($\perp$) MSRDs of the first coordination shell of copper and germanium.

In the case of germanium, the value quoted for $\nu_E^{\perp}$ is different from the value quoted by Dalba *et al.* (1999), where (10) was used instead of (11).

	$\nu_E^{\parallel}$	$\nu_E^{\perp}$
Cu	4.95 ± 0.05	4.6 ± 0.2
Ge	7.6 ± 0.1	4.1 ± 0.1

of diamond, which allows more intense perpendicular relative vibrations, and is probably related to the negative thermal expansion observed in germanium below 40 K. As a consequence of this high perpendicular/parallel ratio, the Einstein frequency for the perpendicular MSRD is much lower than that for the parallel MSRD. The comparison with the phonon DOS of germanium (Nelin & Nilsson, 1972) suggests that the high-frequency optical modes contribute primarily to the parallel MSRD, while for the perpendicular MSRD the low-frequency acoustic modes play a more determinant role. This kind of consideration can be important, for example, to qualitatively recognize the importance of low-energy transverse acoustic modes in negative thermal expansion materials.

6. Conclusions

In this work the correlated Einstein and Debye models for the EXAFS parallel MSRD have been derived within the general framework of the harmonic approximation for crystals, without *ad hoc* assumptions. The widespread expressions of the two models, which are generally based on simple phenomenological considerations, are thus established on firmer grounds, allowing a better evaluation of their strengths and limitations. In particular, the lack of physical meaning of the Debye correlated model in the case of crystals with more than one atom per primitive cell, already experimentally observed for germanium, is demonstrated on general grounds.

The procedure adopted for the parallel MSRD allowed a straightforward extension of the Einstein and Debye models to the case of the perpendicular MSRD. Both models implicitly assume isotropy: as a consequence they would give a perpendicular MSRD that is always twice the parallel MSRD and the same frequencies. However, accurate experimental data on simple crystals have shown a degree of anisotropy in the relative atomic vibrations, that is non-negligible in copper and very significant in germanium. Consequently, the parallel and perpendicular MSRDs are best-fitted by different Einstein or Debye frequencies (or temperatures).

The comparison of the Einstein frequencies with phonon DOS is far from trivial. However, in some cases it allows a qualitative evaluation of the different contribution of phonon branches to parallel and perpendicular MSRDs.

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