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Acta Cryst. (1972). **A28**, 512

On the Interpretation of Anisotropic Temperature Factors

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(Received 24 April 1972)

A lattice-dynamical formulation of the anisotropic vibration tensors of the atoms in a crystal is presented which may contribute to a better understanding of how the interatomic thermal coupling is expressed in the anisotropic temperature factors.

Introduction

In many instances the atoms in a crystal are linked by strong forces so that one may expect the thermal motions of the individual atoms to be coupled. An obvious example is given by the rigid-body motions of largely rigid molecules. The Debye-Waller factor, however, only refers to one particular atom and there are no cross terms in the expressions for the structure factor and the Bragg intensity which would explicitly account for the coupling of the thermal motions of different atoms in the unit cell. On the other hand, the good results obtained with many molecular structures, which have been refined with thermal rigid-body parameters, show that the Debye-Waller factor is appropriate in its present form. This means that the coupling of the thermal motions of different atoms in the crystal

is correctly accounted for by the structure factor and thus by the Debye-Waller factors of the individual atoms. How does this take place?

In the historical context our problem may be pictured as follows. In 1913 Debye derived the temperature factors by assuming that the motions of the different atoms in the crystal are not coupled. After becoming acquainted with Born & von Karman's (1913) paper on the dynamics of crystal lattices, in which the interatomic forces were taken into account, Debye (1914) derived the temperature factor anew. The surprising result was that the temperature factor for the Bragg intensities did not change its form [*cf.* James (1948), the derivations in Chapters I, 3b and V,1]. On the other hand, Faxen (1918) was able to show that the expression for the thermal diffuse scattering changed pronouncedly by introducing the interatomic forces

into the calculation. For the Debye–Waller factors, however, the apparent paradox arose that the same formalism held for two different physical situations: coupled and uncoupled thermal motions of the atoms. That this is nevertheless true will be illustrated in this paper.

A joint representation of the atomic vibration tensors

We will begin with the lattice-dynamical expression for the Debye–Waller factor as it is known in the literature, *e.g.* Cochran & Cowley (1967), equation (14.4). Let e^{-Mr} be the temperature factor for the r th atom, then

$$M_r(\mathbf{Q}) = \frac{1}{2m_r N} \sum_{\mathbf{q}j} [\mathbf{Q} \cdot \mathbf{e}(r|\mathbf{q}j)]^2 \frac{\hbar\omega_j(\mathbf{q})}{\omega_j^2(\mathbf{q})} \cdot \bar{n}(\mathbf{q}j) + \frac{1}{2}, \quad (1)$$

where the symbols have the following meanings:

$\mathbf{Q} = 2\pi\mathbf{h}$, \mathbf{h} = vector in the reciprocal lattice,

\mathbf{q} : wave vector of a lattice wave,

$j = 1 \dots 3n$: index to the branches of \mathbf{q} ,

n : number of atoms in the unit cell,

$\mathbf{e}(r|\mathbf{q}j)$: vector of polarization of mode $\mathbf{q}j$, which specifies the motions of atom r in this mode,

\hbar : Planck's constant h divided by 2π ,

$\omega_j(\mathbf{q})$: frequency of mode $\mathbf{q}j$ times 2π ,

$\bar{n}(\mathbf{q}j)$: mean quantum number of mode $\mathbf{q}j$ in thermal equilibrium.

m_r : mass of atom r ,

N : number of cells in the crystal.

If one refers $\mathbf{h} = \mathbf{Q}/2\pi$ to an orthonormal basis, multiplying out $[\mathbf{Q} \cdot \mathbf{e}(r|\mathbf{q}j)]^2$ gives nine terms, $2\pi^2 h_i h_k$, in the Debye–Waller factor

$$\exp(-2\pi^2 \sum_{ik} U_r^{ik} h_i h_k). \quad (2)$$

$i, k = 1, 2, 3$ denote the directions of space. The Cartesian components U_r^{ik} of the symmetric tensor U_r have the dimension \AA^2 , whereas the Cartesian components h_i have the dimension \AA^{-1} . With the energy

$$\begin{aligned} \bar{E}(\mathbf{q}j) &= \hbar\omega_j(\mathbf{q})[\bar{n}(\mathbf{q}j) + \frac{1}{2}] \\ &= \frac{1}{2}\hbar\omega_j(\mathbf{q}) \coth\left(\frac{\hbar\omega_j(\mathbf{q})}{2k_B T}\right) \end{aligned} \quad (3)$$

of the mode $\mathbf{q}j$ in thermal equilibrium, one obtains from equations (1), (2), and (3)

$$\begin{aligned} U_r^{ik} &= \frac{1}{2m_r N} \sum_{\mathbf{q}j} \frac{\bar{E}(\mathbf{q}j)}{\omega_j^2(\mathbf{q})} \\ &\times [e_i(r|\mathbf{q}j)e_k^*(r|\mathbf{q}j) + e_i^*(r|\mathbf{q}j)e_k(r|\mathbf{q}j)]. \end{aligned} \quad (4)$$

The asterisk denotes the conjugate complex quantity. (In tensor notation the indices i and k in e_i and e_k should be superscripts. However, we do not attach any tensorial meaning to the position of the indices in this paper.) k_B is Boltzmann's constant and T the absolute temperature. From equations (3) and (4) we obtain an

expression for the case $i=k$, which has already been given by Maradudin, Montroll and Weiss [1963, equation (7.3.5)].

Because equation (4) refers only to one single atom, its form does not permit any conclusions regarding the question of the coupling of the thermal motions of different atoms in the unit cell. Thus we have to search for an expression which comprises all atoms of the unit cell. We shall show that such an expression can be derived in terms of the dynamical matrices of the crystal and that it allows us to discuss our introductory question.

In order to keep the equations concise we first use the high temperature approximation

$$\bar{E}(\mathbf{q}j) = k_B T \quad (5)$$

and extend the results thus obtained below. We insert equation (5) into (4) and also make use of the fact that the $e_i(r|\mathbf{q}j)$ are the components of the eigenvectors which belong to the eigenvalues $\omega_j^2(\mathbf{q})$ of the mass-normalized dynamical matrices $\mathbf{M}(\mathbf{q})$. These matrices are hermitian and of order $3n \times 3n$, *cf. e.g.* Cochran & Cowley [1967, equations (5.8) and (5.11)]. Hence we build up unitary matrices $\mathbf{R}(\mathbf{q})$ of order $3n \times 3n$ with the elements $e_i(r|\mathbf{q}j)$ and diagonal matrices $\mathbf{\Lambda}(\mathbf{q})$ of order $3n \times 3n$ with elements $\omega_j^2(\mathbf{q})$. Then

$$\mathbf{M} = \mathbf{R}\mathbf{\Lambda}\tilde{\mathbf{R}} \quad (6)$$

holds for all wave vectors \mathbf{q} , with $\tilde{\mathbf{R}} = \mathbf{R}^{-1}$, *i.e.* \mathbf{R} is unitary ($\tilde{}$ denotes the conjugate complex transpose matrix, -1 the inverse). From equation (6) follows

$$\mathbf{M}^{-1} = \mathbf{R}\mathbf{\Lambda}^{-1}\tilde{\mathbf{R}}. \quad (7)$$

Since \mathbf{M} and \mathbf{M}^{-1} are mass normalized we multiply equation (4) by the factor m_r and now introduce a mass-normalized mean-square amplitude matrix \mathbf{D} of order $3n \times 3n$. The 3×3 diagonal blocks of \mathbf{D} are the matrices $m_r U_r$, the off-diagonal blocks are 3×3 matrices $\sqrt{m_r m_s} U_{rs}$ which cannot be determined from diffraction data. With the use of equation (5), the extension of equation (4) to a $3n \times 3n$ matrix expression for the n atoms in the unit cell is

$$\mathbf{D} = \frac{k_B T}{2N} \sum_{\mathbf{q}} [\mathbf{M}^{-1}(\mathbf{q}) + \mathbf{M}^{*-1}(\mathbf{q})]. \quad (8)$$

Now we remove the mass normalization in the vibration tensors by means of a transformation \mathbf{Q} . \mathbf{Q} is diagonal of order $3n \times 3n$ and has three elements $1/\sqrt{m_r}$ for the r th atom. With

$$\mathbf{U} = \mathbf{Q}\mathbf{D}\mathbf{Q}^T \quad (9a)$$

and

$$\mathbf{L}^{-1} = \mathbf{Q}\mathbf{M}^{-1}\mathbf{Q}^T \quad (9b)$$

we obtain by analogy with equation (8)

$$\mathbf{U} = \frac{k_B T}{2N} \sum_{\mathbf{q}} [\mathbf{L}^{-1}(\mathbf{q}) + \mathbf{L}^{*-1}(\mathbf{q})]. \quad (10a)$$

\mathbf{U} is a $3n \times 3n$ mean-square amplitude matrix in \AA^2 units, and \mathbf{L} the dynamical matrix which is not mass normalized. Since there is a vector $-\mathbf{q}$ to each wave vector \mathbf{q} we can shorten equation (10a) in the sum over all wave vectors to

$$\mathbf{U} = \frac{k_B T}{N} \sum_{\mathbf{q}} \mathbf{L}^{-1}(\mathbf{q}). \quad (10b)$$

So far, equations (2) and (10) have been referred to a Cartesian coordinate system; they are, however, valid in any coordinate system. In equation (10) the 3×3 diagonal blocks are the vibration tensors \mathbf{U}_r of equation (2). The dynamical matrices $\mathbf{L}(\mathbf{q})$ contain the interatomic force constants for the various couples of atoms in the crystal, *cf. e.g.* Cochran & Cowley [1967, equations (5.8) and (5.11)]. Thus the direct interactions between two reference atoms r and s in one unit cell ($r \neq s$) and in different unit cells are expressed in the off-diagonal blocks of the dynamical matrices $\mathbf{L}(\mathbf{q})$. If there is no interaction among all couples of atoms in the crystal, which are represented by the atoms r and s in the unit cell, then the off-diagonal blocks r, s of the matrices $\mathbf{L}(\mathbf{q})$ are zero for all wave vectors \mathbf{q} .

Our introductory question may now be answered as follows: in equation (10), the mean-square amplitude matrix \mathbf{U} is proportional to the sum of the *inverse* dynamical matrices $\mathbf{L}(\mathbf{q})$. Hence the information, concerning the interactions of atoms r and s in the crystal, contained in the off-diagonal blocks of the matrices $\mathbf{L}(\mathbf{q})$, is transferred into the diagonal blocks \mathbf{U}_r , $r = 1 \dots n$, of the matrix \mathbf{U} by the process of matrix inversion. No matter what the actual values of the off-diagonal blocks of the matrices $\mathbf{L}(\mathbf{q})$ may be they nevertheless affect the actual values of the vibration tensors \mathbf{U}_r . If there is no interaction among any atoms which are not translationally identical, then the matrices $\mathbf{L}(\mathbf{q})$ are all block-diagonal and so is the matrix \mathbf{U} ; hence, in this case the vibration tensors \mathbf{U}_r express the motions of n independent Bravais arrays. Thus, by interpreting the equations (10), we see why the Debye-Waller factors of the individual atoms are sufficient to cope with any situation of coupling in the motions of the atoms in the crystal.

Extension to low temperatures

In the case of low temperatures T or high frequencies $\omega_j(\mathbf{q})$, our previous discussion remains essentially valid although some modifications occur in the equations. These modifications might be introduced by using the series expansion of the coth function in equation (3); the corresponding expansion in terms of force constant matrices was first given by Cyvin (1968). The disadvantage of this expansion lies in the fact that it is only valid in the range

$$\frac{\hbar\omega}{2k_B T} < \pi, \quad (11)$$

thus, in particular, it does not hold for $T=0^\circ\text{K}$ and at room temperature for frequencies higher than about 1270 cm^{-1} . Therefore we use a different approach: we shall show that there is a matrix representation which corresponds to equation (10) but which carries a matrix product $\mathbf{L}^{-1} \mathbf{\Omega}$ instead of \mathbf{L}^{-1} . We insert $\bar{E}(\mathbf{q}, j)$ of equation (3) into equation (4) and define a $3n \times 3n$ diagonal matrix $\mathbf{\Gamma}(\mathbf{q})$ with elements $\Gamma_j(\mathbf{q}) = \bar{E}(\mathbf{q}, j)$. Then in place of the equations (7) and (8) we obtain

$$\mathbf{D} = \frac{1}{2N} \sum_{\mathbf{q}} (\mathbf{R}\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\bar{\mathbf{R}} + \mathbf{R}^*\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\bar{\mathbf{R}}^*)_{\mathbf{q}}. \quad (12)$$

Now, for each wave vector \mathbf{q}

$$\mathbf{R}\mathbf{\Lambda}^{-1}\mathbf{\Gamma}\bar{\mathbf{R}} = \mathbf{R}\mathbf{\Lambda}^{-1}\bar{\mathbf{R}}\mathbf{\Gamma}\bar{\mathbf{R}} = \mathbf{M}^{-1}\mathbf{R}\mathbf{\Gamma}\bar{\mathbf{R}}, \quad (13)$$

and we remove the mass normalization by a transformation \mathbf{Q} , as given by equation (9b), to obtain

$$\begin{aligned} \mathbf{Q}\mathbf{M}^{-1}\mathbf{R}\mathbf{\Gamma}\bar{\mathbf{R}}\mathbf{Q}^T &= \mathbf{L}^{-1}\{\mathbf{Q}^T^{-1}\mathbf{R}\mathbf{\Gamma}(\mathbf{Q}^T^{-1}\mathbf{R})^{-1}\} \\ &= \mathbf{L}^{-1}\mathbf{\Omega}. \end{aligned} \quad (14)$$

$\mathbf{\Omega}$, the expression in curly brackets, is not hermitian. It has the dimension of energy. Instead of equation (10b) we finally obtain

$$\mathbf{U} = \frac{1}{N} \sum_{\mathbf{q}} \mathbf{L}^{-1}(\mathbf{q})\mathbf{\Omega}(\mathbf{q}). \quad (15)$$

Equation (15) is valid for all temperatures and frequencies. For $T > 0^\circ\text{K}$ one may put $\mathbf{\Omega}(\mathbf{q}) = k_B T \mathbf{\Omega}'(\mathbf{q})$ which leads to a formulation that corresponds in greater detail to equation (10b). For high temperatures $\mathbf{\Omega}'$ converges towards the unit matrix. Although introducing the matrix $\mathbf{\Omega}$ into equation (15) modifies the terms in the sum over all \mathbf{q} , our discussion of the mechanism of the coupling is not essentially invalidated since the inversion $\mathbf{L} \rightarrow \mathbf{L}^{-1}$ is not annulled by the factor $\mathbf{\Omega}$.

Interpretation of the atomic temperature factors

In section 2 we have shown that the coupling of the thermal motions of a reference atom r in the unit cell with the motions of the other atoms in the crystal is expressed in the vibration tensor \mathbf{U}_r . Thus we may regard the vibration tensor \mathbf{U}_r as summing up the concerted dynamical impacts of the 'environments' of the r th atom in the crystal. What is missing, however, in the vibration tensor \mathbf{U}_r is a detailed account of how the motions of the atom r are coupled with the motions of a neighbouring atom s in the unit cell. This information is contained in the 3×3 off-diagonal blocks \mathbf{U}_{rs} of the matrix \mathbf{U} . Although these blocks are uniquely defined by the dynamical matrices of the crystal they cannot be determined by experiment. For in the equations for X-ray scattering the explicit coupling terms, referring to different atoms in the crystal, do not enter into the expression for the lattice spectra but

only into the expression for the thermal diffuse scattering, cf. Cochran & Cowley (1967, equation 14.3). Although the off-diagonal blocks U_{rs} cannot be determined experimentally they can nevertheless be used to formulate the equations for the thermal bond-length correction in lattice-dynamical terms, which we shall do in a forthcoming paper.

In order to achieve a more detailed interpretation of the tensors U_r , it is thus necessary to develop dynamical models which describe the average motions of the atoms in the unit cell. Such models can be suggested by chemical information and the details of the given static structure. The models should then explain the observed values of the vibration components U_r^{ik} to a certain extent, and depending how correct, complete and accurate the model is, one obtains information on the thermal coupling of different atoms. As a rule such models will only be rough approximations, and in many cases we have no (external) means to prove that they are correct and are the only ones possible. The models may easily be incorrect when the components U_r^{ik} are not pronouncedly anisotropic or when the number of determined components U_r^{ik} is too small. (A further source of error is, of course, given by the often low accuracy with which the vibration components are determined.)

The simplest 'models' which were applied in the past only imply that magnitude and direction of the principal vibration components of an atom fit well to the geometrical arrangement of the neighbouring atoms. This has been found to hold with many structures. Thus with layer structures, the smallest vibration amplitudes of atoms in the layer are often parallel to the layer whereas the largest ones are perpendicular to it. Similarly, with many inorganic structures the principal vibration amplitudes are found to point in distinct directions of the coordination polyhedra, and the magnitudes of the principal vibrations are found to correspond to the free space left in those directions. As an example of a more involved dynamical model derived from the static structure we quote Megaw's (1970) analysis of the dynamics of the calcite structure, which ex-

plains the unexpected directions of the largest principal vibration amplitudes of the oxygen atoms. A model which has frequently been used to calculate bond-length corrections, is the riding model proposed by Busing & Levy (1964). All these models suffer from the fact that they are established purely from structural evidence and that no external (numerical) checks are at our disposal. An exception in this regard is the model of the rigid-body vibrations which can often be applied to nearly rigid molecules or ions. Since this model can be described by an explicit set of appropriate parameters which can be refined from the components U_r^{ik} of the atoms of the molecule or from intensity data, there are several criteria which allow one to examine the validity of the rigid-body model on a numerical basis, see e.g. Cruickshank, Pilling, Bujosa, Lovell & Truter (1961); Burns, Ferrier & McMullan (1968); and Pawley (1972).

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