allel to $(111)_A$ between two cubic crystals A and B with a misorientation θ about [011]. Since the axis of misorientation is a twofold axis of symmetry, rotations of angles θ and $(180° - \theta)$ are equivalent. Fig. 1 shows, for each value of θ $(0 < \theta \leq 90°)$, the angles of tilt and twist which correspond to the equivalent description involving the smallest angle of tilt or twist. The maximum deviation from a pure case is $16 \cdot 9°$ and occurs for $\theta = 29 \cdot 5°$. Pure-tilt boundaries occur for the following values of θ: $39 \cdot 0$, $50 \cdot 5$ and $70 \cdot 5°$.

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The Coupling of the Thermal Motions of the Atoms in a Crystal as Deduced from the Acoustic Spectrum of the Thermal Diffuse Scattering

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The strength of the coupling of the motions of the atoms in different cells of a crystal is investigated by means of the acoustic spectrum of the thermal diffuse scattering. The calculations are performed for a monatomic cubic crystal. Correlation coefficients, which express the amount of in-phase motions of remote atoms in the crystal, are approximately determined from the term $1/q^2$ of the acoustic spectrum. This term is valid for all crystals. We find that the coupling of the motions of the atoms is approximately inversely proportional to the distance between the atoms in the crystal.

1. Introduction

In the usual lattice-dynamical treatment of the thermal motions of the atoms it is assumed that there are forces among the atoms in the crystal so that the motions of the atoms are coupled. This assumption means that the internal motions of a lattice can be represented by a superposition of separate running or standing waves (in the harmonic approximation). In such a wave all atoms move with the same frequency and a phase shift which is determined by the wavelength and the position of the atom in the crystal. Hence, for such a wave a coupling of the motions of even widely separated atoms in the crystal exists. In a crystal with many cells there are as many waves which are excited according to the laws of quantum statistics. Because of the different wavelengths the superposition of the waves in the motions of any particular atom prevents a noticeable effect of thermal coupling between widely separated atoms in the crystal. This means that in the crystal two atoms show a noticeable in-phase (or out-of-phase) motion only within a certain distance. Now we want to know how large this distance is, or to what extent the coupling of the motions of the atoms decreases with increasing distance.

The interatomic thermal coupling becomes manifest in the acoustic spectrum of the thermal diffuse scattering, which shows sharp maxima at the reciprocal-lattice points. Thus it should be possible to draw conclusions about the strength of the interatomic coupling

from the profile of the acoustic spectrum. Such an attempt will be made in this paper. We restrict our treatment to a monatomic cubic crystal and only discuss the manifest acoustic spectrum of the first order.

2. Derivation of the coupling terms

The intensity of the first-order acoustic spectrum for a monatomic cubic lattice is given by

$$I(S/\lambda) = f_0^2 e^{-2M} \sum_n \sum_m \sum_{qj} G_{qj} \exp \{2\pi i \, S/\lambda$$
$$\times (\mathbf{r_n} - \mathbf{r_m})\} \cos \{\mathbf{q} \cdot (\mathbf{r_n} - \mathbf{r_m})\}, \quad (1)$$

where

$$\sum_{qj} G_{qj} = 2M; \quad (2)$$

and for temperatures well above the Debye temperature

$$G_{qj} = \frac{k_B T}{mN \omega_j^2(\mathbf{q})} \left[\frac{2\pi}{\lambda} \, \mathbf{S} \cdot \mathbf{e}(\mathbf{q}j) \right]^2, \quad (3)$$

(*cf.* James, 1948, equations 5·27, 5·23 and 5·25). The symbols have the following meaning:

λ = wavelength of the X-rays,
S/λ = vector in reciprocal space, $S = |\mathbf{S}| = 2 \sin \theta$,
f_0 = scattering factor for the atom at rest,
$\mathbf{n}, \mathbf{m}$ = indices to denote the cell in the crystal; the components n_l and m_l are integer,

$\mathbf{r_n}, \mathbf{r_m}$ = vectors from the origin to the cells $\mathbf{n}$, $\mathbf{m}$, referred to an orthonormal metric,

$\mathbf{q}$ = wave vector of a lattice wave,

$\mathbf{e}(\mathbf{q}j)$ = unit vector of the wave $\mathbf{q}$ in the direction j of polarization; $j = 1, 2, 3$,

$\omega_j(\mathbf{q})$ = circular frequency of mode $\mathbf{q}j$,

k_B = Boltzmann's constant,

T = absolute temperature,

m = mass of the atoms,

N = number of cells (atoms) in the crystal.

For a monatomic crystal with $N_1 N_2 N_3 = N$ cells there are $3N$ lattice modes $\mathbf{q}j$ and as many first-order diffuse maxima in the first Brillouin zone. Since the diffuse maxima overlap to a large extent, because of their finite line width, the exact values of N_1, N_2, N_3 do not matter and I_1 is often represented as a continuous function. Using $|\mathbf{q}| = q$, $\mathbf{q} = 2\pi\mathbf{g}$, and $|\mathbf{g}| = g = 1/\lambda(\mathbf{q})$ = magnitude of the wave vector $\mathbf{g}$ in $Å^{-1}$ units, $V_{\mathbf{q}j} = \omega_j(\mathbf{q})/q$ = velocity of wave $\mathbf{q}j$, α_{sj} = angle between $\mathbf{S}/\lambda$ and $\mathbf{e}(\mathbf{q}j)$,

we obtain

$$I(\mathbf{S}/\lambda) = f_0^2 \, e^{-2M}\sigma, \qquad (4)$$

where

$$\sigma \equiv N^2 \sum_{j=1}^{3} G_{\mathbf{q}j}, \qquad (5)$$

which can be shown to be

$$\sigma = \frac{k_B T}{mg^2} \left(\frac{S}{\lambda}\right)^2 \sum_{j=1}^{3} \frac{\cos^2 \alpha_{sj}}{V_{\mathbf{q}j}^2}, \qquad (6)$$

(cf. James, 1948, equations 5·36, 5·40, and 5·44).

Since the lattice waves occur only in the term

$$\sum_{\mathbf{q}j} G_{\mathbf{q}j} \cos\{\mathbf{q} \cdot (\mathbf{r_n} - \mathbf{r_m})\} \qquad (7)$$

of equation (1) we conclude that this term accounts for the fact that there is thermal coupling between the cells (atoms) $\mathbf{n}$ and $\mathbf{m}$ in the crystal. Thus our investigation is first concerned with the expression (7) which we denote by $T_{\mathbf{n}-\mathbf{m}}$. We simplify it by carrying out the summation over j. With equations (5) and (7) we then obtain

$$T_{\mathbf{n}-\mathbf{m}} = \frac{1}{N^2} \sum_{\mathbf{g}} \sigma(\mathbf{g}) \cos\{2\pi\mathbf{g} \cdot (\mathbf{r_n} - \mathbf{r_m})\}. \qquad (8)$$

According to equation (6) $\sigma(\mathbf{g})$ is a continuous function of g and therefore we proceed to integration in equation (8). For this purpose we need the volume element in $\mathbf{g}$ space. With a^* as the lattice constant of the cubic reciprocal lattice the density of points in the $\mathbf{g}$ lattice is N/a^{*3}, and hence the volume element is Nd^3g/a^{*3}. Furthermore, with equation (6) $\sigma(\mathbf{g})/N$ does not depend on N, the number of cells in the crystal. We put $\sigma(\mathbf{g})/N \equiv \varepsilon(\mathbf{g})$. With equation (8) we now obtain

$$T_{\mathbf{n}-\mathbf{m}} = \frac{1}{a^{*3}} \int_{\substack{\text{Brillouin} \\ \text{zone}}} \varepsilon(\mathbf{g}) \cos\{2\pi\mathbf{g} \cdot (\mathbf{r_n} - \mathbf{r_m})\} d^3g. \qquad (9)$$

Since $G_{\mathbf{q}j}$ and $\varepsilon(\mathbf{g})$ are real, $T_{\mathbf{n}-\mathbf{m}}$ is also real. Obviously

$$T_{\mathbf{n}-\mathbf{m}} = T_{\mathbf{m}-\mathbf{n}} \qquad (10)$$

by virtue of equation (9). In the following we abbreviate $T_{\mathbf{n}-\mathbf{m}} \equiv T_{\mathbf{nm}}$.

Now we want to express $\varepsilon(\mathbf{g})$ as a function of the coupling terms $T_{\mathbf{nm}}$, i.e. we look for the transformation inverse to that of equation (9). For this purpose we introduce $\mathbf{g}$ in equation (1) by using the relation $\mathbf{S}/\lambda = \mathbf{S_0}/\lambda + \mathbf{g}$, where $\mathbf{S_0}/\lambda$ is the vector to a reciprocal lattice point. Since

$$\exp\{2\pi i \, \mathbf{S_0}/\lambda \cdot (\mathbf{r_n} - \mathbf{r_m})\} = 1,$$

we now obtain

$$\exp\{2\pi \, i \, \mathbf{S}/\lambda \cdot (\mathbf{r_n} - \mathbf{r_m})\}$$
$$= \exp\{2\pi \, i \, \mathbf{g} \cdot (\mathbf{r_n} - \mathbf{r_m})\} \qquad (11)$$

for each pair of cells $\mathbf{m}$ and $\mathbf{n}$. We divide equation (1) by $f_0^2 \, e^{-2M}$, use $T_{\mathbf{nm}}$ instead of the expression (7) and obtain from equation (1)

$$\sigma(\mathbf{g}) = \sum_{\mathbf{n}} \sum_{\mathbf{m}} T_{\mathbf{nm}} \exp\{2\pi \, i \, \mathbf{g} \cdot (\mathbf{r_n} - \mathbf{r_m})\}. \qquad (12)$$

As an intensity $\sigma(\mathbf{g})$ must be real; this is expressed formally by equation (10). Because of equation (10) $\sigma(\mathbf{g})$ is also symmetric with respect to a reciprocal lattice point.* If one refers $\sigma(\mathbf{g})$ to the unit cell we obtain by virtue of equation (10)

$$\varepsilon(\mathbf{g}) = \frac{1}{N} \sum_{\mathbf{n}} \sum_{\mathbf{m}} T_{\mathbf{nm}} \cos\{2\pi\mathbf{g} \cdot (\mathbf{r_n} - \mathbf{r_m})\}. \qquad (13)$$

$\varepsilon(\mathbf{g})$ only depends on the differences $\mathbf{r_n} - \mathbf{r_m}$ but not on the single vectors $\mathbf{r_n}$ and $\mathbf{r_m}$. For an infinitely large lattice, $N \to \infty$, all differences occur with equal frequency, N times in the limit. If we count each difference $\mathbf{r_n} - \mathbf{r_m} \equiv \Delta\mathbf{r_{nm}}$ only once, and take into account its frequency of occurrence, we obtain from equation (13)

$$\varepsilon(\mathbf{g}) = \sum_{\Delta\mathbf{r_{nm}} = -\infty}^{+\infty} T_{\mathbf{nm}} \cos\{2\pi \, \mathbf{g} \cdot \Delta\mathbf{r_{nm}}\}$$

$$= \sum_{\Delta\mathbf{n} = -\infty}^{+\infty} T_{\mathbf{nm}} \cos\left\{\frac{2\pi}{a^*} \sum_{l=1}^{3} g_l \, \Delta n_l\right\}, \qquad (14)$$

where the $\Delta n_l = n_l - m_l$ are integers. If we also express equation (9) by $\Delta\mathbf{r_{nm}}$ we obtain

$$T_{\mathbf{nm}} = \frac{1}{a^{*3}} \int_{\substack{\text{Brillouin} \\ \text{zone}}} \varepsilon(\mathbf{g}) \cos\{2\pi\mathbf{g} \cdot \Delta\mathbf{r_{nm}}\} d^3g. \qquad (15)$$

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* James (1948, equation 5.44 and p. 211) states that $\sigma(\mathbf{g})$ is *not* centrosymmetric with respect to a reciprocal lattice point – in contrast to our result. Our result is a direct consequence of our equation (1), whereas James deduces the asymmetry of $\sigma(\mathbf{g})$ from his equation (5.44). In deriving (5.44), however, it is assumed that $\mathbf{S}/\lambda$ is constant throughout the Brillouin zone (integration in equation 5.39). The asymmetry of $\sigma(\mathbf{g})$ only arises when this assumption is dropped. The centrosymmetry of $\sigma(\mathbf{g})$ is also found by Laue (1960, p. 249).

Thus we have the following result: The coupling terms T_{nm}, referring to two atoms m and n in the crystal, are the Fourier transforms of the intensity of the acoustic spectrum per unit cell, when the factor $f_0^2 e^{-2M}$ is not taken into account. On the other hand the intensity per unit cell can be represented by a Fourier series in Δr space with the coupling terms T_{nm} as Fourier coefficients. Thus $\varepsilon(g)$ and T_{nm} are real Fourier inverse to each other.*

Although a Fourier summation occurs in equation (14) the intensity distribution $\varepsilon(g)$ is, of course, not periodic; the summation is only a consequence of the summation over all cells in equation (1). Rather $\varepsilon(g)$ is not equal at each reciprocal-lattice point (in each Brillouin zone) because $\varepsilon(g)$ also depends on the reciprocal lattice vector S/λ, as shown by equation (6). Therefore the coupling terms T_{nm} are different for each Brillouin zone in reciprocal space. Furthermore, since equation (6) is only valid for $|S/\lambda| \gg g$, our equations (14) and (15) also only hold under this condition; i.e. the Brillouin zones considered should lie far outside in reciprocal space. These restrictions on our results cannot be eliminated and they unfortunately prevent the coupling terms T_{nm}, which only describe the specific crystal, from being calculated from the acoustic spectrum in a direct manner.

In order to control our previous calculations we now show, by comparison with the known equations for uncoupled motions of the atoms in the crystal, that the quantities T_{nm} have their origin in the coupling of the motions. For uncoupled motions the intensity of the thermal background is given by

$$I_u = f_0^2 N(1 - e^{-2M})$$
$$= f_0^2 e^{-2M} N\{2M + \tfrac{1}{2}(2M)^2 + \ldots\}, \quad (16)$$

(cf. James, 1948, equation 1·35). The first term in the series expansion corresponds to the first-order acoustic spectrum. Hence, for uncoupled motions, we have from the first term

$$\varepsilon_u(g) = I_u(\text{1st term})/f_0^2 e^{-2M} N = 2M . \quad (17)$$

In our notation no coupling means $T_{nm} = 0$ for all

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* This relation has an obvious parallel. The equations (14) and (15) correspond to the equations for the Fourier synthesis of the electron-density distribution with positive and real coefficients. Equation (10) corresponds to Friedel's law. Formally the roles of direct and reciprocal space are exchanged however: in equation (15) we integrate the cell contents $\varepsilon(g)$, multiplied with a phase factor, over the unit cell in reciprocal space in order to gain the 'structure amplitude' T_{nm} which occurs in direct space. On the other hand, the Fourier summation (14) is carried out in reciprocal space with the coefficients T_{nm} of direct space. A further difference with respect to the Fourier representation of the electron density consists of the fact that in equation (15) the integration is performed over intensities and not over amplitudes. Thus the coefficients T_{nm} represent the maxima of a 'squared crystal' (cf. Buerger, 1959). But the maxima T_{nm} differ from the maxima of a Patterson synthesis in that they do not refer to the interatomic vectors within the unit cell but rather to those within the lattice, and in that the interatomic vectors all have the same multiplicity (in an infinitely large crystal).

$n \neq m$ and $T_{nn} \neq 0$. The terms with $n = m$ denote the coupling of one and the same atom, which we abbreviate by T_0. From equation (15) we obtain

$$T_0 = \frac{1}{a^{*3}} \int_{\substack{\text{Brillouin} \\ \text{zone}}} \varepsilon(g) \, d^3 g . \quad (18)$$

From equation (18) we deduce that $T_0 = 2M$, which is established from the equations (2), (5) and (18) as follows:

$$2M = \sum_{qj} G_{qj} = \sum_g \sigma(g)/N^2$$

$$= \frac{N}{a^{*3}} \int_{\substack{\text{Brillouin} \\ \text{zone}}} \sigma(g)/N^2 d^3 g = T_0 .$$

First we show that, with $T_0 = 2M$ and $T_{nm} = 0$ for $n \neq m$, our equations yield the result (17) for uncoupled motions: If we insert $T_{nm} = 0$ and $T_0 = 2M$ in equation (13) we obtain

$$\varepsilon(g) = \frac{1}{N} \sum_n 2M = 2M ,$$

which is identical with the result (17). On the other hand, if we insert $\varepsilon(g) = 2M$ in equation (15) we obtain $T_0 = 2M$ and $T_{nm} = 0$ for $n \neq m$. Hence $T_{nm} \neq 0$ is a necessary and sufficient condition for the coupling of the motions of different atoms in the crystal.

3. Calculation of correlation coefficients

Since the coupling terms T_{nm} depend on the choice of the reciprocal lattice point considered, i.e. on S/λ, our equations do not allow one to calculate values of T_{nm} which describe only the particular crystal. We can improve the situation by calculating average values; the average being taken either over all vectors S/λ or over the squared velocities V_{qj}^2 of the lattice modes. In the first case the terms $\cos^2 \alpha_{sj}$ in equation (6) become approximately $\tfrac{1}{3}$ because of $\sum \cos^2 \alpha_{sj} = 1$, and one can perform the calculation with different velocities of sound (or with different elastic constants). The advantage of this type of calculation is that the particular properties of the crystal are taken into account. In the second case, with an average velocity of sound, the dependence on S/λ vanishes, since $\sum \cos^2 \alpha_{sj} = 1$ for all vectors S/λ, but some of the specific properties of the crystal are lost. One obtains an acoustic spectrum according to

$$\varepsilon(g) = \frac{C}{g^2} , \quad (19)$$

where C is a constant, which depends only on the magnitude of S/λ, the mass of the atoms, the temperature and the average velocity of sound, cf. equation (6). The simple spectrum, according to equation (19) has the advantage that we can approximately calculate the coupling terms T_{nm}, as follows.

We regard the Brillouin zone as a sphere about the reciprocal lattice point (in reality it is a cube for a

cubic lattice), introduce polar coordinates and obtain with equations (15) and (19)

$$T_{nm} = \frac{C4\pi}{a^{*3}} \int_0^{g_{max}} \frac{\sin(2\pi g \, \Delta r_{nm})}{2\pi g \, \Delta r_{nm}} \, dg, \qquad (20)$$

(cf. International Tables for X-ray Crystallography, 1959, p. 73). g and Δr_{nm} are referred only to the radial direction of the sphere. The value of g_{max} is determined from the condition that the volume of the cubic and spherical forms of the Brillouin zone should be equal. We obtain $g_{max} = 0.620 \, a^*$ Å^{-1}. To a sufficient approximation we assume that a and a^* can also be regarded as 'lattice constants' in the radial direction. Then Δr_{nm} has the values $(0, 1, 2 \ldots) \, a$. The integration in equation (20) can now be carried out and we find

$$T_{nm} = \frac{C \, 4\pi}{a^{*3} \, 2\pi \, \Delta r_{nm}} \text{Si}(2\pi \, \Delta r_{nm} \, 0.620a^*), \qquad (21)$$

where the function $\text{Si}(x)$ represents the sine integral. Values of $\text{Si}(x)$ are given in the tables of Abramowitz & Stegun (1965, p. 227). For $\Delta r_{nm} = a$ we obtain $\text{Si}(2\pi \, 0.620) = 1.776$, which comes already close to the limit of $\pi/2 = 1.571$, to which $\text{Si}(x)$ converges quickly for values of $\Delta r_{nm} > 5a$. For $\Delta r_{mn} = 0$ we immediately obtain from equation (20)

$$T_0 = C \, 4\pi \, 0.620/a^{*2}. \qquad (22)$$

Hence the correlation coefficients are

$$V_{nm} \equiv \frac{T_{nm}}{T_0} = \frac{\text{Si}(2\pi \, \Delta r_{nm} \, 0.620 \, a^*)}{2\pi \, \Delta r_{nm} \, 0.620a^*}, \qquad (23)$$

with $V_0 = 1$. If we insert the limit $\pi/2$ for the sine integral and use $g_{max} = \frac{1}{2}$, which is somewhat too small, we obtain the even members of the harmonic series

$$V_{nm} = 1, \tfrac{1}{2}, \tfrac{1}{4}, \tfrac{1}{6}, \ldots \qquad (24)$$

when Δr_{nm} attains the values $(0, 1, 2, 3, \ldots) \, a$. The correlation coefficients are always positive, which means that the atoms move primarily with similar phases. This result is reasonable since the long acoustic waves are more excited in thermal equilibrium than the short ones and thus primarily determine the phases. According to equations (23) and (24) the coupling of the motions of the atoms in the crystal decreases comparatively slowly, more or less inversely proportional to their distance. This slow decrease of the interatomic coupling is, however, remarkable since the interatomic forces normally decrease rapidly with a high power of the interatomic distance. But we can understand this

result by considering that the coupling terms T_{nm} express the gross effect of interatomic coupling, i.e. the effect that arises when the coupling between remote atoms in the crystal is established through a number of nearest-neighbour and other possible interactions.

Our result (24) satisfies a formal condition which must be fulfilled for the uniform convergence of the Fourier series of equation (14), (cf. Tolstow, 1955, p. 91). The coefficients T_{nm} converge to zero with increasing Δr_{nm}. Furthermore, the decrease of the coupling terms according to equation (24) justifies an (incorrect) assumption which we made in deriving equation (14): for finite crystals the differences Δr_{nm} are less frequent for the larger distances. Since the coupling terms for large distances are small, the large distances have only a small weight in the series (14) and an incorrect assumption about the frequency of their occurrence has no marked effect on the result.

We emphasize that our results (21) and (24) are derived only from the characteristic factor $1/g^2$ of the acoustic spectrum. Hence these equations are approximately valid for all crystals. How well the strength of the interatomic coupling for a particular crystal is represented by the equations (21) and (24) depends on how much the velocities of sound deviate from each other in the different directions of space. If one wants to obtain more exact results for a particular crystal one has to carry out the calculations with the actual velocities of sound and for several reciprocal-lattice points (with large values of S/λ). This leads to complicated three-dimensional Fourier transformations. We believe, however, that, with our simple calculation, we have determined the basic trend of the coupling of the thermal motions of the atoms in the crystal as a function of increasing distance.

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