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## Thermally Excited Forbidden Reflections\*

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Methods have been developed for predicting the thermal excitation of certain structurally forbidden reflections in simple crystals. The excitation of these reflections is related to the anharmonicity and anisotropy of the atomic thermal motion. The methods are illustrated by their application to the cuprite and *A15* structures. New extinction rules for these reflections are derived, and their structure factors are given in terms of the thermal parameters of the structures.

### Introduction

The experimental observation of very weak Bragg maxima forbidden by the structure in simple crystals dates from W. H. Bragg's (1921) measurement of the 222 reflection of diamond. Early attempts to understand and interpret this anomaly in the diffraction pattern of diamond include those of Renninger (1935) and Pisharoty (1941). More recent work (Renninger, 1955; Götlicher & Wölfel, 1959; Renninger, 1960; Demarco & Weiss, 1965; and Colella & Merlini, 1966) has extended the observation to silicon and germanium and has included a determination (Roberto & Batterman, 1970) of the unusual temperature dependence of this reflection. The phenomenon is now understood to be partly due to the noncentrosymmetric electron distribution about the atomic sites in elements with the diamond structure and partly to the anharmonic character of the thermal motion in this structure. That there is a contribution to the intensity from thermal motion is evident from the neutron measurements of Keating, Nunes, Batterman & Hastings (1971). The measurements of Trucano & Batterman (1972) of the 442 reflection in silicon extend the phenomenon to

the general class of structurally forbidden reflections for which  $h$ ,  $k$ , and  $l$  are all even but nonzero, and  $h+k+l=2(2p+1)$ . Their intensity data as a function of temperature also show that the effects of electron distribution and thermal motion tend to oppose each other, leading to a characteristic temperature at which the intensity of the 442 vanishes.

In spite of the attention given to thermally excited forbidden reflections in the diamond structure, to the writer's knowledge they have not been studied in any other crystal. It is our purpose here to suggest that the phenomenon may be fairly common, to provide a basis for predicting which of the structurally forbidden Bragg maxima are excited, and to develop methods for interpreting their integrated intensities in terms of the thermal parameters of the crystal. For simplicity we will omit diffraction effects related to nonspherical atomic electron distributions, taking the atomic scattering factor to be real and isotropic in reciprocal space. The development is illustrated by its application to cuprite and the *A15* structure, a prototype for which is the intermetallic compound  $\text{Nb}_3\text{Sn}$ .

### Forbidden reflections in cuprite

The mineral cuprite,  $\text{Cu}_2\text{O}$ , is cubic with two formula weights per cell. The space group is  $Pn3m$  and there are

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four copper atoms in special positions  $b$  (0,0,0; 0,  $\frac{1}{2}$ ,  $\frac{1}{2}$ ;  $\frac{1}{2}$ , 0,  $\frac{1}{2}$ ;  $\frac{1}{2}$ ,  $\frac{1}{2}$ , 0) and two oxygen atoms in special positions  $a \pm (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ . Hence without regard to thermal motion its structure factor is

$$F_{hkl} = f_{\text{Cu}} \{1 + \exp [\pi i(h+k)] + \exp [\pi i(h+l)] + \exp [\pi i(k+l)]\} + 2f_0 \cos \frac{\pi}{2} (h+k+l), \quad (1)$$

and if  $h$ ,  $k$ , and  $l$  are mixed and have an odd sum,  $F_{hkl} = 0$ . If we view thermal motion as a dynamic perturbation of the periodicity of the crystal, we expect the sharp features of the intensity distribution in reciprocal space, the Bragg maxima, to be determined by the average structure. Hence in general we may write for the time averaged structure factor

$$\langle F_{hkl} \rangle = \sum_n f_n \exp [i\mathbf{k} \cdot \mathbf{r}_n] \langle \exp [i\mathbf{k} \cdot \delta_n] \rangle. \quad (2)$$

Here  $\delta_n$  is a small time-dependent displacement vector of the  $n$ th atom in the unit cell from its average position  $\mathbf{r}_n$  and  $\mathbf{k}$  is the diffraction vector times  $2\pi$ . A consequence of the harmonic approximation is that  $\langle \exp [i\mathbf{k} \cdot \delta_n] \rangle = \exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle]$ , which is the usual harmonic Debye-Waller factor. Since we are here concerned with possible effects associated with anharmonicity, we choose to write without approximation

$$\langle \exp [i\mathbf{k} \cdot \delta_n] \rangle = \exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle] \times \langle \exp [\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle + i\mathbf{k} \cdot \delta_n] \rangle. \quad (3)$$

The second exponential on the right of (3) is the anharmonicity factor. Any deviation of that quantity from unity is a manifestation of the anharmonic character of the thermal motion. Since in general  $\langle \mathbf{k} \cdot \delta_n \rangle = 0$ , its series expansion may be written

$$\begin{aligned} \langle \exp [\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle + i\mathbf{k} \cdot \delta_n] \rangle \\ = 1 - \frac{1}{6} i \langle (\mathbf{k} \cdot \delta_n)^3 \rangle - \frac{1}{8} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle^2 + \frac{1}{24} \langle (\mathbf{k} \cdot \delta_n)^4 \rangle \\ - \frac{1}{12} i \langle (\mathbf{k} \cdot \delta_n)^2 \rangle \langle (\mathbf{k} \cdot \delta_n)^3 \rangle + \frac{1}{120} i \langle (\mathbf{k} \cdot \delta_n)^5 \rangle + \dots \end{aligned}$$

In what follows it is convenient to assume that  $\delta_n$  is sufficiently small that we may neglect terms of power higher than three in  $\mathbf{k} \cdot \delta_n$ . It will be clear, however, that the subsequent development may be readily modified to accommodate as many such terms as experiment may indicate useful. To this approximation, then, equation (2) becomes

$$\langle F_{hkl} \rangle = \sum_n f_n \exp [i\mathbf{k} \cdot \mathbf{r}_n] \times \exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle] \{1 - \frac{1}{6} i \langle (\mathbf{k} \cdot \delta_n)^3 \rangle\}. \quad (4)$$

We note that the approximation used in equation (4) automatically causes the thermal motion of an atom whose environment is centrosymmetric to be treated as harmonic, since in that case the average of any odd power of  $\mathbf{k} \cdot \delta_n$  must vanish.

We consider the contribution to the average structure factor of cuprite, of the copper atom at the origin. Since the origin is a center of symmetry for  $\text{Cu}_2\text{O}$ , it

must be simply  $f_{\text{Cu}} \exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle]$ . With

$$\delta_n = x_n \mathbf{a}_1 + y_n \mathbf{a}_2 + z_n \mathbf{a}_3,$$

$x_n$ ,  $y_n$ , and  $z_n$  being small time-dependent pure numbers and the  $\mathbf{a}_m$ 's being the unit-cell vectors in real space, and

$$\mathbf{k} = 2\pi(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3), \quad (6)$$

the  $\mathbf{b}_m$ 's being vectors reciprocal to the  $\mathbf{a}_m$  triplet, we have

$$\begin{aligned} \frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle = 2\pi^2 \{h^2 \langle x_n^2 \rangle + k^2 \langle y_n^2 \rangle + l^2 \langle z_n^2 \rangle \\ + 2hk \langle x_n y_n \rangle + 2kl \langle y_n z_n \rangle + 2lh \langle z_n x_n \rangle\}. \quad (7) \end{aligned}$$

For the atom at the origin, with two oxygen neighbors at  $\pm (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , we must have that  $\langle x_n^2 \rangle = \langle y_n^2 \rangle = \langle z_n^2 \rangle$ . However, since the principal axes of its anisotropic thermal ellipsoid (the point symmetry of its environment is  $\bar{3}m$ ) do not correspond to the cube axes, the cross terms of (7) do not vanish. Given, say, a positive value of  $x_n$ ,  $y_n$  will tend to be negative because of the oxygen atom at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ .

Introduce the notation  $M_{\text{Cu}} = 2\pi^2 \langle x_n^2 \rangle (h^2 + k^2 + l^2)$ , the isotropic part of the Debye-Waller factor, and

$$-Q = 4\pi^2 \langle x_n y_n \rangle = 4\pi^2 \langle y_n z_n \rangle = 4\pi^2 \langle z_n x_n \rangle.$$

Then

$$\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle = M_{\text{Cu}} - Q(hk + kl + lh)$$

and with  $Q$  treated as small,

$$\exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle] = [1 + Q(hk + kl + lh)] \exp [-M_{\text{Cu}}]. \quad (8)$$

Because its trigonal axis is in a  $[11\bar{1}]$  direction, for the copper site at  $(\frac{1}{2}, \frac{1}{2}, 0)$ , we must have that

$$\langle x_n y_n \rangle = -\langle y_n z_n \rangle = -\langle z_n x_n \rangle.$$

For it, a result analogous to equation (8) is

$$\exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle] = [1 + Q(hk - kl - lh)] \exp [-M_{\text{Cu}}].$$

After a similar consideration of the remaining two copper sites in the unit cell, we find for the total copper contribution to the average structure factor

$$\begin{aligned} F_{\text{Cu}} = f_{\text{Cu}} \exp [-M_{\text{Cu}}] \{ [1 + Q(hk + kl + lh)] \\ + [1 + Q(hk - kl - lh)] \exp [\pi i(h+k)] \\ + [1 + Q(-hk - kl + lh)] \exp [\pi i(h+l)] \\ + [1 + Q(-hk + kl - lh)] \exp [\pi i(k+l)] \}. \quad (9) \end{aligned}$$

If the indices are unmixed, to within the approximations here used, equation (9) reduces to the conventional result,  $F_{\text{Cu}} = 4f_{\text{Cu}} \exp [-M_{\text{Cu}}]$ , and there is no diffraction effect resulting from the anisotropy of the copper thermal motion. However, for mixed indices, with  $l$  taken as the index of different parity, equation (9) becomes

$$F_{\text{Cu}} = 4f_{\text{Cu}} Q h k \exp [-M_{\text{Cu}}]. \quad (10)$$

The cubic point symmetry of the oxygen sites ( $\bar{4}3m$ ) causes equation (7) to reduce to a simple isotropic

form:

$$\frac{1}{2}\langle(\mathbf{k} \cdot \delta_n)^2\rangle = 2\pi^2\langle x_n^2\rangle(h^2 + k^2 + l^2) = M_0. \quad (11)$$

However these sites are not symmetry centers so that the anharmonicity factor of equation (3) or (4) must be considered. With the aid of equations (5) and (6), we find that

$$\begin{aligned} \frac{1}{6}\langle(\mathbf{k} \cdot \delta_n)^3\rangle &= \frac{4\pi^3}{3} \{h^3\langle x_n^3\rangle + k^3\langle y_n^3\rangle + l^3\langle z_n^3\rangle \\ &+ 3hk^2\langle x_n y_n^2\rangle + 3kl^2\langle y_n z_n^2\rangle + 3lh^2\langle z_n x_n^2\rangle \\ &+ 3h^2k\langle x_n^2 y_n\rangle + 3k^2l\langle y_n^2 z_n\rangle + 3l^2h\langle z_n^2 x_n\rangle \\ &+ 6hkl\langle x_n y_n z_n\rangle\}. \end{aligned} \quad (12)$$

Since it is evident that positive and negative values of  $x_n$ ,  $y_n$ , and  $z_n$  for the oxygen atoms are equally likely, it follows that  $\langle x_n^3\rangle = \langle y_n^3\rangle = \langle z_n^3\rangle = 0$ . Since it is also evident that for a given  $y_n$ , positive and negative  $x_n$  are equally likely, we have that  $\langle x_n y_n^2\rangle = 0$ . Similarly the remaining terms of (12) vanish except that which contains the factor  $\langle x_n y_n z_n\rangle$ .

Hence with  $S = 8\pi^3\langle x_n y_n z_n\rangle$  for the oxygen atom at  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , its contribution to the average structure factor is  $f_0 \exp[-M_0] \exp[\pi i/2(h+k+l)](1 - iShkl)$ . That the effect of anharmonicity in the thermal motion of a tetrahedrally coordinated atom should be of this form has been pointed out by Willis (1969).

Since the environment of the site  $(\frac{3}{4}, \frac{3}{4}, \frac{3}{4})$  is anti-symmetric to that of  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ , the contribution of its occupant to the structure factor must be  $f_0 \exp[-M_0] \exp[-\pi i/2(h+k+l)](1 + iShkl)$ , and the total oxygen contribution is

$$F_0 = 2f_0 \exp[-M_0] \left\{ \cos \frac{\pi}{2}(h+k+l) + Shkl \sin \frac{\pi}{2}(h+k+l) \right\}. \quad (13)$$

Combination of equations (10) and (13) gives for the structurally forbidden reflections, those for which  $h$  and  $k$  are even,  $l$  odd, and  $h+k+l=4q \pm 1$ ,

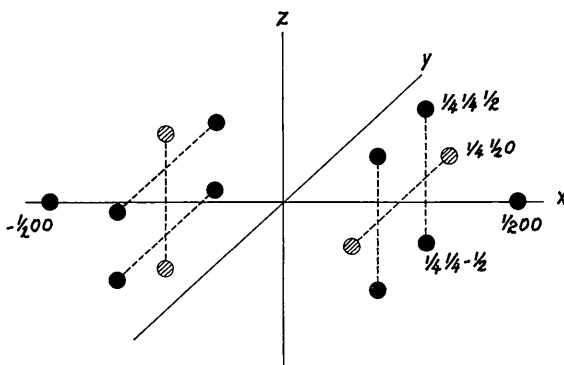


Fig. 1. A schematic representation of the nearest twelve neighbors of the  $A$  site  $\frac{1}{4}, 0, \frac{1}{2}$  in the  $A15$  structure.  $A$  atoms are shown as full circles and  $B$  atoms are shaded. The  $x$  axis is expanded relative to  $y$  and  $z$  for the sake of clarity.

$$\langle F_{hkl} \rangle = 2hk\{2f_{Cu}Q \exp[-M_{Cu}] \pm f_0 S l \exp[-M_0]\}. \quad (14)$$

### Forbidden reflections in the $A15$ structure

Compounds with the  $A15$  structure type (*Strukturbericht*, 1937) are ideally of the form  $A_3B$  with two formula weights in a cubic cell and space group  $Pm\bar{3}n$ . Six  $A$  atoms occupy special positions  $c$  (point symmetry  $\bar{4}2m$ ):  $\frac{1}{4}, 0, \frac{1}{2}$ ;  $\frac{1}{2}, \frac{1}{4}, 0$ ;  $0, \frac{1}{2}, \frac{1}{4}$ ;  $\frac{3}{4}, 0, \frac{1}{2}$ ;  $\frac{1}{2}, \frac{3}{4}, 0$ ;  $0, \frac{1}{2}, \frac{3}{4}$ ; and there are two  $B$  atoms in special positions  $a$  (point symmetry  $m\bar{3}$ ):  $0, 0, 0$ ;  $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ . If we neglect thermal effects the structure factor is

$$\begin{aligned} F_{hkl} &= f_B \{1 + \exp[\pi i(h+k+l)]\} + f_A \{ \exp[\pi i(h/2+l)] \\ &\times (1 + \exp[\pi ih]) + \exp[\pi i(k/2+h)](1 + \exp[\pi ik]) \\ &+ \exp[\pi i(l/2+k)](1 + \exp[\pi il]) \}. \end{aligned} \quad (15)$$

There are two general classes of  $hkl$  for which  $F_{hkl}$  vanishes: (1)  $h$ ,  $k$ , and  $l$  are all odd. (2) One index is odd and the other two are both multiples of four, or one is odd and the other two are both odd multiples of two.

The two  $B$  sites are both centrosymmetric with cubic environments, hence their contribution to the time average of the structure factor is

$$F_B = f_B \exp[-M_B] \{1 + \exp[\pi i(h+k+l)]\},$$

where  $M_B = 2\pi^2\langle x_n^2\rangle(h^2 + k^2 + l^2)$ . To our approximations they make no contributions to forbidden reflections and are of no further interest.

However the  $A$  sites are not symmetry centers and their point symmetry is only tetragonal. Therefore we may expect effects resulting both from the anharmonic and anisotropic character of the thermal motion of their occupants.

We consider the thermal motion of the occupant of the site  $(\frac{1}{4}, 0, \frac{1}{2})$ . It has two  $A$  nearest neighbors at  $a_0/2$ , four  $B$  next nearest neighbors at  $a_0\sqrt{5}/4$ , and eight  $A$  next nearest neighbors at  $a_0/6/4$ . This array about the site is illustrated schematically in Fig. 1.

In order to compute the various averages in equation (12) it is useful to introduce a probability density function  $P(xyz)$  such that  $P(xyz)dxdydz$  is the probability that the relevant atom be found within the volume element at coordinates  $xyz$  in the sense of equation (5). In terms of it we have

$$\langle x^p y^q z^r \rangle = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} x^p y^q z^r P(xyz) dx dy dz. \quad (16)$$

We of course do not know  $P$ , but from the environment of the site under consideration, we know some of its symmetry properties. Since it is evident from Fig. 1 that the  $xy$  and  $xz$  planes are mirror planes it follows that

$$P(xyz) = P(x\bar{y}z) = P(xy\bar{z}) = P(x\bar{y}\bar{z}). \quad (17)$$

It is also clear from the figure that the character of the  $yz$  plane is such that  $P$  is recovered upon reversal of

the sign of  $x$ , provided that the coordinates  $y$  and  $z$  are interchanged. Hence

$$P(xyz) = P(\bar{x}zy) = P\bar{x}z\bar{y} = P(\bar{x}\bar{z}y) = P(\bar{x}\bar{z}\bar{y}) . * \quad (18)$$

Since from equations (18)  $\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} P(xyz)dydz$  must be an even function of  $x$ , for  $q=r=0$  and  $p$  odd equation (16) is zero; hence  $\langle x^3 \rangle = 0$ . Similarly, from equations (17)  $\langle y^3 \rangle = \langle z^3 \rangle = 0$ . Also from (17), since

$$\int_{-\infty}^{+\infty} zP(xyz)dz = \int_{-\infty}^{+\infty} yP(xyz)dy = 0,$$

for  $q$  or  $r=1$  equation (16) vanishes. So

$$\langle x^2y \rangle = \langle x^2z \rangle = \langle y^2z \rangle = \langle z^2y \rangle = \langle xyz \rangle = 0.$$

We now consider  $\langle y^2x \rangle$ .

$$\begin{aligned} \langle y^2x \rangle &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} y^2xP(xyz)dxdydz \\ &= \int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} y^2xP(xyz)dxdydz \\ &\quad - \int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} y^2xP(\bar{x}yz)dxdydz . \end{aligned} \quad (19)$$

By equations (18) the second integral on the right of (19) is

$$\begin{aligned} &\int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} y^2xP(\bar{x}yz)dxdydz \\ &= \int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} y^2xP(xzy)dxdydz \\ &= \int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} z^2xP(xyz)dxdydz . \end{aligned}$$

So equation (19) becomes

$$\langle y^2x \rangle = \int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (y^2 - z^2)xP(xyz)dxdydz$$

which is not zero since  $P(xyz) \neq P(xzy)$ . By a similar argument we have that  $\langle z^2x \rangle = -\langle y^2x \rangle$ , and equation (12) reduces to

$$\frac{1}{6} \langle (\mathbf{k} \cdot \delta_n)^3 \rangle = 4\pi^3 \langle y_n^2 x_n \rangle h(k^2 - l^2) . \quad (20)$$

We consider the anisotropy of the thermal motion of the atom at  $(\frac{1}{4}, 0, \frac{1}{2})$ . From the properties of  $P$  given by equations (17) and (18) there results

$$\langle xy \rangle = \langle yz \rangle = \langle zx \rangle = 0$$

and

$$\langle x^2 \rangle \neq \langle y^2 \rangle = \langle z^2 \rangle .$$

So equation (7) becomes

$$\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle = 2\pi^2 \{ \langle x_n^2 \rangle h^2 + \langle y_n^2 \rangle (k^2 + l^2) \} = M_A + \alpha h^2$$

\* Symmetry properties of  $P$  analogous to equations (17) and (18) for an oxygen atom in cuprite are  $P(xyz) = P(\bar{x}\bar{y}\bar{z}) = P(\bar{x}y\bar{z}) = P(x\bar{y}\bar{z}) = P(yxz) = P(zyx) = P(xzy)$ . But  $P(xyz) \neq P(\bar{x}yz)$  and  $P(xyz) \neq P(\bar{x}\bar{y}\bar{z})$ .

where

$$M_A = 2\pi^2 \langle y_n^2 \rangle (h^2 + k^2 + l^2)$$

and

$$\alpha = 2\pi^2 (\langle x_n^2 \rangle - \langle y_n^2 \rangle) .$$

Hence with  $\alpha$  small,

$$\exp [-\frac{1}{2} \langle (\mathbf{k} \cdot \delta_n)^2 \rangle] = \exp [-M_A] (1 - \alpha h^2) . \quad (21)$$

Combination of equations (20) and (21) gives for the contribution of the  $A$  atom at  $(\frac{1}{4}, 0, \frac{1}{2})$  to the average structure factor

$$f_A \exp [\pi i(h/2 + l)] \exp [-M_A] \{1 - \alpha h^2 - i\beta h(k^2 - l^2)\}$$

where

$$\beta = 4\pi^3 \langle y_n^2 x_n \rangle .$$

From the symmetry of the atomic arrangement about it,  $\langle (\mathbf{k} \cdot \delta_n)^3 \rangle$  for the  $A$  atom at  $\frac{3}{4}, 0, \frac{1}{2}$  must simply be the negative of that quantity given by equation (20), but  $\langle (\mathbf{k} \cdot \delta_n)^2 \rangle$  must be the same for both sites. Hence the contribution to the average structure factor from the occupant of site  $(\frac{3}{4}, 0, \frac{1}{2})$  is

$$f_A \exp [\pi i(3h/2 + l)] \exp [-M_A] \{1 - \alpha h^2 + i\beta h(k^2 - l^2)\} .$$

Similar considerations of the remaining  $A$  sites yields for the total contribution to the average structure factor

$$\begin{aligned} F_A &= 2f_A \exp [-M_A] \{ \exp [\pi i(h + l)] [(1 - \alpha h^2) \\ &\quad \times \cos(\pi h/2) - \beta h(k^2 - l^2) \sin(\pi h/2)] \\ &\quad + \exp [\pi i(k + h)] [(1 - \alpha k^2) \cos(\pi k/2) - \beta k(l^2 - h^2) \\ &\quad \times \sin(\pi k/2)] + \exp [\pi i(l + k)] [(1 - \alpha l^2) \cos(\pi l/2) \\ &\quad - \beta l(h^2 - k^2) \sin(\pi l/2)] \} . \end{aligned} \quad (22)$$

For the class of forbidden reflections for which  $h, k$ , and  $l$  are all odd, from equation (22) we have

$$\begin{aligned} \langle F_{hkl} \rangle &= -2\beta f_A \exp [-M_A] \{ h(k^2 - l^2) \sin(\pi h/2) \\ &\quad + k(l^2 - h^2) \sin(\pi k/2) + l(h^2 - k^2) \sin(\pi l/2) \} . \end{aligned} \quad (23)$$

For those forbidden reflections for which, say,  $h$  is odd and  $k$  and  $l$  are both even multiples of two, or both odd multiples of two, there results

$$\begin{aligned} \langle F_{hkl} \rangle &= 2f_A (k^2 - l^2) \exp [-M_A] \\ &\quad \times \{ \beta h \sin(\pi h/2) + \alpha \cos(\pi k/2) \} . \end{aligned} \quad (24)$$

## Discussion

Our treatment of the anomalous contribution of thermal motion to the structure factor for cuprite indicates that most of the structurally forbidden Bragg maxima (those for which two indices are even and one odd) remain extinguished. In order that the reflection be thermally excited, from equation (14), neither of the even indices may be zero. For  $h^2 + k^2 + l^2 \leq 30$  (approximately the limit for Cu  $K\alpha$  radiation), of the twelve forbidden reflections, only four are thermally excited. From equation (14), their structure factors are

$$\langle F_{221} \rangle = 16f_{\text{Cu}}Q \exp[-M_{\text{Cu}}] + 8f_0S \exp[-M_0], \quad (25)$$

$$\langle F_{223} \rangle = 16f_{\text{Cu}}Q \exp[-M_{\text{Cu}}] - 24f_0S \exp[-M_0], \quad (26)$$

$$\langle F_{421} \rangle = 32f_{\text{Cu}}Q \exp[-M_{\text{Cu}}] - 16f_0S \exp[-M_0], \quad (27)$$

$$\langle F_{423} \rangle = 32f_{\text{Cu}}Q \exp[-M_{\text{Cu}}] + 48f_0S \exp[-M_0]. \quad (28)$$

We note that three of the excited reflections have extinguished companions with common  $h^2+k^2+l^2$ : 221 (003), 223 (401), and 423 (205). Measurement of each reflection with its companion may be useful to insure that any observed intensity is not related to extraneous contributions such as the Renninger effect. With a knowledge of the atomic scattering factors and Debye-Waller factors, equations (25)–(28) may be used to determine the magnitudes and relative signs of the thermal parameters  $Q$  and  $S$ .

Though the forbidden reflections fall into two classes for the *A15* structure, the criterion for their remaining extinguished is common to them all. From equations (23) and (24) we see that any forbidden reflection for which two of the indices are the same has zero average structure factor. Note from the equations that this criterion is relevant only to the magnitudes of the indices and not their signs. As in the case of cuprite, most of the reflections are not excited.

For the class of forbidden reflections in the *A15* structure for which all indices are odd, there are five with  $h^2+k^2+l^2 < 100$  which are thermally excited, three of which have extinguished companions: 531, 731 (553), 751 (555), 753 (911), and 931. From equation (23), their intensities depend only on the anharmonicity parameter  $\beta$ .

For the second class of reflections whose structure factors are given by equation (24), there are fourteen thermally excited Bragg maxima with  $h^2+k^2+l^2 < 100$ . They are listed with their structure factors and forbidden companions in Table 1. Note that there are two sets of three reflections – 740, 180, 562; and 762, 580, 384 – such that each of the three is the same distance from the origin in reciprocal space. From either of these triplets, a measurement of their relative intensities yields the relative magnitudes and signs of the thermal parameters  $\alpha$  and  $\beta$  without a knowledge of either  $f_A$  or  $M_A$ .

Table 1. *Thermally excited forbidden reflections in the A15 structure for which one index is odd and two are even*

<i>hkl</i>	$h^2+k^2+l^2$	$\langle F_{hkl} \rangle$ ( $f_A \exp[-M_A]$ )	Companion extinguished <i>hkl</i>
140	17	32 ( $\beta+\alpha$ )	322
340	25	32 ( $-3\beta+\alpha$ )	500
162	41	64 ( $\beta-\alpha$ )	344
540	41	32 ( $5\beta+\alpha$ )	
362	49	64 ( $-3\beta-\alpha$ )	700
740	65	32 ( $-7\beta+\alpha$ )	none
180	65	128 ( $\beta+\alpha$ )	
562	65	64 ( $5\beta-\alpha$ )	166
380	73	128 ( $-3\beta+\alpha$ )	
184	81	96 ( $\beta+\alpha$ )	900, 744, 366
762	89	64 ( $-7\beta-\alpha$ )	922
580	89	128 ( $5\beta+\alpha$ )	
384	89	96 ( $-3\beta+\alpha$ )	566
940	97	32 ( $9\beta+\alpha$ )	

It is important to emphasize that the effects related to nonspherical atomic electron distributions, for which the atomic scattering factor may be complex and anisotropic in reciprocal space, have been omitted from our considerations. The results from diamond suggest that such effects may not be negligible. Such contributions to the forbidden reflections may be avoided by the use of neutrons.

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