

absorption coefficient of the shower producing radiation. However, for much greater thicknesses of lead it seems necessary to adopt the view that the showers occasioned by the air secondaries do not reach the ionization chamber and that the burst-producing radiation originates in the lead, probably as a result of a close nuclear approach of a high energy primary. On this view any barometer effect would have to be due to the air absorption of the primary particles and should therefore be much smaller than for bursts involving air secondaries.

Burst frequency as a function of shield thickness

The shield of 17 cm of lead shot ordinarily used on the meters described above is apparently thick enough to absorb a considerable portion of the burst-producing radiation and resultant burst particles. Evidence for this is a very considerable, at least twofold, increase in burst frequency which ensues when a few hundred pounds of the shot is drained out.³¹ The optimum shield thickness to give maximum burst fre-

³¹ R. L. Doan, *Phys. Rev.* **48**, 470 (1935).

quency has not yet been determined but probably lies in the neighborhood of five cm of lead. This corresponds to a similar situation in the case of showers, where the frequency increases with additional top shielding up to about 2 cm of lead and then falls off for greater thicknesses. The size of the bursts seems not to be greatly affected by reducing the shield thickness.

In conclusion the writer wishes to acknowledge his great indebtedness to Professor A. H. Compton for providing the opportunity of making this investigation and also for numerous suggestive discussions during its progress. Thanks are also due to the Carnegie Institution of Washington through whom the necessary funds were provided, and to Dr. J. A. Fleming, Director of the Institution, who emphasized the desirability of such a comparative study. Practically all of the statistical calculations presented here and many more that have not been discussed were carried out by Mrs. Ardis T. Monk with the help of J. O. Pyle, Jr., and James Geary. Needless to say, this assistance has been invaluable from the standpoint of expediting the investigation.

Theory of the Effect of Temperature on the Reflection of X-Rays by Crystals

II. Anisotropic Crystals

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In anisotropic crystals the temperature factor for the reflection of x-rays is a function of the orientation of the reflection plane. The general case of anisotropic metals is here treated by an extension of a simple method recently discussed in this journal. The complete solution is found for metals with hexagonal symmetry. The temperature

factor is generally written as e^{-M} . The constant M is explicitly calculated for Zn and Cd (hexagonal symmetry). It is found that for these two metals M is 1.80, 1.73, respectively, as large for the reflection plane normal to the principal axis as for reflection planes parallel to the principal axis.

§1. INTRODUCTION

IN view of the approximations made in the Debye theory of specific heats, its success for isotropic as well as for anisotropic crystals is surprising. An explanation may lie in the relative

insensitiveness of the specific heat to the assumptions made about the lattice vibrations. In particular, the specific heat is a scalar quantity, and so does not directly reflect the anisotropic vibrations of the atoms in anisotropic metals. This anisotropy in vibrations may, however, be detected experimentally by a study of the temperature dependence of the atomic

* The author was aided in part by a grant from the Rockefeller Foundation to Washington University for research in science.

structure factor in the reflection of x-rays. Thus the mean square displacement μ of an atom along a definite direction, parallel say to the unit vector \mathbf{n} , is related by the formula¹

$$M = 8\pi^2\mu \sin^2 \theta / \lambda^2 \quad (1)$$

to the temperature factor e^{-M} for the reflection of x-rays from planes normal to \mathbf{n} .

The purpose of this paper is to show how the mean square displacement μ depends upon direction in single crystals of metals not having cubic symmetry.

Assuming only that the amplitudes of vibration are sufficiently small so that the potential energy of the metal may be regarded as a quadratic function of the displacement, one obtains²

$$\mu(\mathbf{n}) = \frac{h}{4\pi^2 M} \sum_{j, \mathbf{k}} \gamma^2(j, \mathbf{k}) \left\{ \frac{1/\nu}{e^{h\nu/kT} - 1} + \frac{1}{2\nu} \right\}. \quad (2)$$

The vector \mathbf{k} specifies a wave having a direction of propagation along the direction of \mathbf{k} , and whose wave-length is $2\pi/k$. The letter j specifies one of the three waves associated with each \mathbf{k} , the three waves corresponding to one longitudinal and two transverse waves in isotropic solids. $\nu(j, \mathbf{k})$ is the classical frequency of the wave (j, \mathbf{k}) . $\gamma^2(j, \mathbf{k})$ is the square of the direction cosine between \mathbf{n} and the direction of vibration of the wave (j, \mathbf{k}) . M is the mass of the crystal. The summation is over all waves in the crystal.

In isotropic metals μ is the same for all directions \mathbf{n} . In anisotropic metals μ is a quadratic function of the components of \mathbf{n} , l , m , n . This is readily seen when we expand

$$\gamma_{j, \mathbf{k}} = ll_{j\mathbf{k}'} + mm_{j\mathbf{k}'} + nn_{j\mathbf{k}'},$$

where $l_{j\mathbf{k}'}$, $m_{j\mathbf{k}'}$, $n_{j\mathbf{k}'}$ are the direction cosines of the direction of vibration of the wave (j, \mathbf{k}) . When the coordinate axes are chosen to lie along the principal axes of the crystal, μ will have the form

$$\mu(\mathbf{n}) = \mu_x l^2 + \mu_y m^2 + \mu_z n^2. \quad (3)$$

¹ Waller and James, Proc. Roy. Soc. **A117**, 214 (1927); Zener and Jauncey, Phys. Rev. **49**, 17 (1936) have given a simple and general proof of this formula.

² Zener and Jauncey, reference 1. The derivation of this formula given in this reference explicitly assumed the Debye model of a solid. However, one need only assume that the motion of an atom may be represented as the superposition of linearly polarized plane elastic waves.

This equation shows directly that μ has rotational symmetry in metals with a three-, four-, or six-fold axis of symmetry. Further, it shows that $\mu(\mathbf{n})$ is completely determined by its three values for \mathbf{n} pointing along the three principal axes. Hence the mean square displacement μ is completely determined by the experimental determination of the temperature factor for the three (sometimes only two) reflection planes normal to the principal axes.

When evaluating the summation in (2), we shall assume that the velocity of the waves is independent of their wave-length. It is well known that this is incorrect for the shortest wave-lengths. However, it is just these short waves with high frequency which contribute least to the sum (2).

If n is the number of atoms per unit volume, and V is the volume of the solid, the total number of terms included in the summation (2) must be $3nV$. In the customary form of the Debye theory of specific heat this number is obtained, for an analogous summation, by excluding all waves with a frequency greater than a critical frequency ν_m . In this paper the correct number will be obtained by excluding all waves with wave-length shorter than a critical value $\lambda(\sigma)$, where σ is a unit vector in the direction of propagation, i.e., it is \mathbf{k}/k . As indicated, this value will in general be a function of the direction of propagation. Only in this manner can we associate, for short as well as for long waves, three directions of vibration for each \mathbf{k} .

The summation over \mathbf{k} in (2) may now be converted into an integral. If $C(j, \sigma)$ is the velocity of a "j" wave with the direction of propagation σ , the number of "j" waves with frequency between ν and $\nu + d\nu$, and having σ within the solid angle $d\Omega$, is $VC^{-3}(j, \sigma)\nu^2 d\nu d\Omega$.³ Introducing the notation $\xi = h\nu/kT$, $x(j, \sigma) = h\nu_m(j, \sigma)/kT = \theta(j, \sigma)/T$, with $\nu_m(j, \sigma) = C(j, \sigma)/\lambda_0(\sigma)$, we obtain

$$\mu = \frac{kTV}{4\pi^2 M} \sum_j \int \frac{\gamma^2(j, \sigma)}{C^2(j, \sigma)\lambda_0(\sigma)} \{ \Phi(x) + x/4 \} d\Omega, \quad (4)$$

where

$$\Phi(x) = - \int_0^x \frac{\xi}{e^\xi - 1} d\xi.$$

³ Jeans, *The Dynamical Theory of Gases* (The University Press, Cambridge, 1925), p. 354.

TABLE I. Quantization factor.

x	$\Phi(x)+x/4$	x	$\Phi(x)+x/4$
0.0	1.000	1.2	1.040
0.2	1.001	1.4	1.054
0.4	1.004	1.6	1.069
0.6	1.010	1.8	1.087
0.8	1.018	2.0	1.107
1.0	1.028	2.5	1.164

The factor $\{\Phi(x)+x/4\}$ represents the effect of quantization. From an inspection of Table I, we see that the quantization effect is only of importance when t is considerably less than the maximum $\Theta(j; \sigma)$.

In order that the correct number of waves be included, $\lambda_0(\sigma)$ must satisfy

$$\int \int_{\lambda_0}^{\infty} \lambda^{-4} d\lambda d\Omega = n, \quad \text{i.e.,} \quad \int \lambda_0^{-3}(\sigma) d\Omega = 3n. \quad (5)$$

If the quantization factor differs inappreciably from unity, as in most metals at room temperature, and if $\lambda_0(\sigma)$ is regarded as independent of σ , we obtain

$$\mu(\mathbf{n}) = \frac{3kT}{4\pi^2 m_a} \sum_i \int \frac{\gamma^2(j, \sigma) d\Omega}{v_0^2(j, \sigma) 4\pi}, \quad (6)$$

where $m_a = M/(nV)$, $v_0(j, \sigma) = C(j, \sigma)/\lambda_0$, with $\lambda_0 = (4\pi/3n)^{1/3}$.

In order to evaluate $\mu(\mathbf{n})$, as given in (4), we must know both the velocity and the direction of vibration associated with each "j" wave for all directions of propagation σ . In this paper we first study in detail the waves in a two-dimensional medium (§2). This analysis is given for two reasons. Firstly, the principles involved are identical with the principles for the three-dimensional case, while the analysis is much shorter. Secondly, the problem for crystals with hexagonal symmetry is reducible to the two-dimensional problem. The formal problem of determining the wave velocities and the directions of vibration in a three-dimensional medium⁴ is then briefly reviewed (§3) and the solution given for metals with hexagonal symmetry. Finally, the numerical results are given (§4) for all the metals with hexagonal symmetry whose

⁴ The theory has been presented in an elegant manner by Kelvin, *Baltimore Lectures* (The University Press, Cambridge, 1904), Lecture XI.

elastic constants have been determined, namely, Zn and Cd.

§2. WAVES IN TWO-DIMENSIONAL MEDIA

Let U, V be the x, y components of the displacement vector of the medium, $X_x, Y_y, Y_x = X_y$ be the stress components, and e_{xx}, e_{yy}, e_{xy} be the strain components. The equations of motion are then⁵

$$\begin{aligned} \delta X_x / \delta x + \delta Y_x / \delta y &= \rho \ddot{U}, \\ \delta Y_x / \delta x + \delta Y_y / \delta y &= \rho \ddot{V}. \end{aligned} \quad (7)$$

The stress components are linear functions of the strain components, i.e.,

$$\begin{aligned} X_x &= c_{11}e_{xx} + c_{12}e_{yy} + c_{13}e_{xy}, \\ Y_y &= c_{12}e_{xx} + c_{22}e_{yy} + c_{23}e_{xy}, \\ Y_x &= c_{13}e_{xx} + c_{23}e_{yy} + c_{33}e_{xy}. \end{aligned} \quad (8)$$

The strain components, in turn, may be expressed in terms of the displacement components by means of the equations

$$e_{xx} = \frac{\delta U}{\delta x}, \quad e_{yy} = \frac{\delta V}{\delta y}, \quad e_{xy} = \frac{\delta U}{\delta y} + \frac{\delta V}{\delta x}. \quad (9)$$

By means of (8) and (9) we may transform (7) into two homogeneous partial differential equations in U and V . If we try as a solution a linearly polarized plane wave, see Fig. 1,

$$(U, V) = (a, b)e^{i\omega(t - (lx + my)/c)}, \quad l^2 + m^2 = 1,$$

these two differential equations reduce to

$$\begin{aligned} \{l^2 c_{11} + 21mc_{13} + m^2 c_{33}\}a \\ + \{lm(c_{12} + c_{32}) + l^2 c_{13} + m^2 c_{23}\}b &= \rho c^2 a, \\ \{lm(c_{12} + c_{33}) + l^2 c_{13} + m^2 c_{23}\}a \\ + \{m^2 c_{22} + 2lmc_{23} + l^2 c_{33}\}b &= \rho c^2 b. \end{aligned} \quad (10)$$

Let c_l and c_t denote the two values of c for which Eqs. (10) have a nontrivial solution, and let c_l be the larger of the two. Further let the corresponding solutions be (a_l, b_l) and (a_t, b_t) . The velocities and the corresponding solutions may readily be found in two extreme cases. When the medium is isotropic ($c_{11} = c_{22}$, $c_{13} = c_{23} = 0$, $2c_{33} = c_{11} - c_{12}$), c_l and c_t are independent of

⁵ Love, *The Mathematical Theory of Elasticity* (The University Press, Cambridge, 1920), p. 83. The notation adopted in this paper is that used by Love.

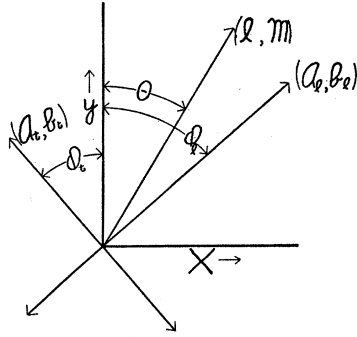


FIG. 1. Vibration directions in anisotropic media. The vector (l, m) is parallel to the direction of propagation. The vectors (a_l, b_l) and (a_t, b_t) are along the directions of vibration.

the direction of propagation, the vector (a_l, b_l) is parallel to the direction of propagation, while the vector (a_t, b_t) is perpendicular to this direction. On the other hand, in the highly anisotropic case $c_{12} = c_{13} = c_{23} = c_{33} = 0$, c_l^2 and c_t^2 form the upper and lower branches, respectively, of two intersecting straight lines when plotted as functions of l^2 . One of the vectors (a_l, b_l) , (a_t, b_t) is parallel to the x axis, one to the y axis. They suddenly interchange directions when $c_l = c_t$, as in Fig. 3. The properties of an actual anisotropic medium will be intermediate between those of these two extreme cases. The interesting case $c_{22} \ll c_{11}$ is illustrated in Fig. 4. c_l^2 and c_t^2 no longer coincide at a critical point, c_l^2 retains a marked variation with l^2 , while c_t^2 varies only slightly, being the same for $l=0$ as for $l=1$. The vectors (a_l, b_l) , (a_t, b_t) change gradually, as for the case of isotropy, but the component of (a_l, b_l) along the axis of least compressibility, here the x axis, is larger on the average than its component along the axis of greatest compressibility.

This apparent preference of (a_l, b_l) for the direction of least compressibility, so marked in the second limiting case of Fig. 3, may be best understood when Eqs. (10) are put into a variational form. Let us write these equations in the form

$$\lambda_{11}a + \lambda_{12}b = \rho c^2 a, \quad \lambda_{12}a + \lambda_{22}b = \rho c^2 b. \quad (11)$$

Multiplying the first equation by a , the second by b , and adding, we obtain

$$\rho c^2 = (\lambda_{11}a^2 + 2\lambda_{12}ab + \lambda_{22}b^2) / (a^2 + b^2). \quad (12)$$

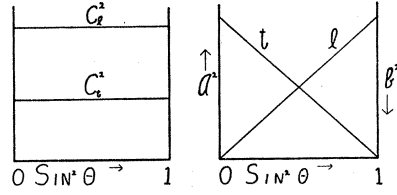


FIG. 2. Isotropic medium. a_l, b_l are the x, y components of the vibration associated with c_l . a_t, b_t are the x, y components of the vibration associated with c_t . c_l is defined as the larger, c_t as the smaller, of the two velocities.

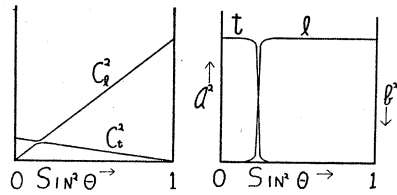


FIG. 3. Highly anisotropic medium. Fig. 2 is reproduced for a medium whose compressibility is much greater along the y axis than along the x axis.

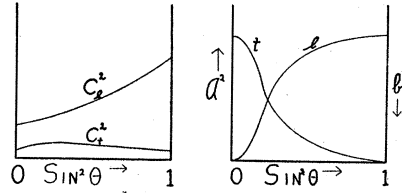


FIG. 4. Moderately anisotropic medium. Fig. 2 is reproduced for a medium which is only slightly anisotropic.

We now regard the left-hand side of this equation as a function of a and b . Eqs. (11) are then equivalent to the statement that c^2 , as given by (12), is an extremum. Now the compressional waves have the greatest velocity when the direction of propagation lies along the axis of least compressibility. It is thus evident that when the direction of propagation (l, m) is not along the axis of least compressibility, then c^2 , as given by (12), will have its maximum for a direction of (a, b) between (l, m) and this axis.

In the following section we shall need analytic expressions for c_l, c_t and the corresponding solutions of (11). These velocities are given by

$$\rho c_l^2 = \frac{\lambda_{11} + \lambda_{22}}{2} + \left\{ \left(\frac{\lambda_{11} - \lambda_{22}}{2} \right)^2 + \lambda_{12}^2 \right\}^{\frac{1}{2}}, \quad (13a)$$

$$\rho c_t^2 = \frac{\lambda_{11} + \lambda_{22}}{2} - \left\{ \left(\frac{\lambda_{11} - \lambda_{22}}{2} \right)^2 + \lambda_{12}^2 \right\}^{\frac{1}{2}}. \quad (13b)$$

Since the two solutions (a_i, b_i) , (a_i, b_i) are orthogonal, $a_i a_i + b_i b_i = 0$, the normalized solutions may be written in the form

$$(a_i, b_i) = (\cos \varphi, \sin \varphi), \quad (a_i, b_i) = (-\sin \varphi, \cos \varphi).$$

The angle φ , Fig. 1, is given by

$$\varphi = \frac{1}{2} \tan^{-1}(2\lambda_{12}/(\lambda_{11} - \lambda_{12})). \quad (14)$$

§3. WAVES IN THREE-DIMENSIONAL MEDIA

The method of calculating the velocity and vibration directions of linearly polarized plane waves in a three-dimensional solid is a trivial extension of the method for a two-dimensional solid. This was discussed in the preceding paragraph. We need only give the results for the three-dimensional solid.

Let us consider a plane wave whose direction of propagation has the direction cosines (l, m, n) with respect to the x, y, z axes. The direction cosines α, β, γ of the vibration direction of this wave, as well as the velocity c of this wave, must satisfy the set of equations

$$\begin{aligned} (A_{11} - \rho c^2)\alpha + A_{12}\beta + A_{13}\gamma &= 0, \\ A_{12}\alpha + (A_{22} - \rho c^2)\beta + A_{23}\gamma &= 0, \\ A_{13}\alpha + A_{23}\beta + (A_{33} - \rho c^2)\gamma &= 0. \end{aligned} \quad (15)$$

The coefficients are given in terms of the elastic constants⁴ by

$$\begin{aligned} A_{11} &= l^2 c_{11} + m^2 c_{66} + n^2 c_{55} + 2lmc_{16} + 2mnc_{56} + 2nlc_{51}, \\ A_{12} &= l^2 c_{16} + m^2 c_{26} + n^2 c_{45} + lm(c_{12} + c_{66}) \\ &\quad + mn(c_{25} + c_{46}) + nl(c_{14} + c_{56}), \\ A_{13} &= l^2 c_{15} + m^2 c_{46} + n^2 c_{35} + lm(c_{14} + c_{56}) \\ &\quad + mn(c_{26} + c_{45}) + nl(c_{13} + c_{55}), \\ A_{22} &= l^2 c_{66} + m^2 c_{22} + n^2 c_{44} + 2lmc_{26} + 2mnc_{24} + 2nlc_{46}, \\ A_{23} &= l^2 c_{56} + m^2 c_{24} + n^2 c_{34} + lm(c_{25} + c_{46}) \\ &\quad + mn(c_{23} + c_{44}) + nl(c_{36} + c_{45}), \\ A_{33} &= l^2 c_{55} + m^2 c_{44} + n^2 c_{33} + 2lmc_{45} + 2mnc_{34} + 2nlc_{35}. \end{aligned}$$

The exact determination of those values of c^2 for which Eqs. (15) have nontrivial solutions usually

involves the solution of a cubic equation, namely, the equation obtained by equating to zero the determinant of the coefficients. There is one case of physical interest, other than the case of isotropy, where an analytical solution may be obtained for the allowed values of c^2 and for the corresponding sets of direction cosines (α, β, γ) . This is the case of hexagonal symmetry about a principal axis. Here⁶ the elastic constants satisfy the same conditions as in the case of rotational symmetry about a principal axis, namely, the following coefficients must vanish:

$$c_{16}, c_{26}, c_{36}, c_{46}, c_{56}, c_{45}, c_{14}, c_{24}, c_{15}, c_{25}, c_{34}, c_{35}$$

and the following relations must hold,

$$c_{11} = c_{22}, \quad c_{13} = c_{23}, \quad c_{44} = c_{55}, \quad c_{66} = (1/2)(c_{11} - c_{12}).$$

An important simplification may now be introduced. Since in this case the elastic constants are invariant with respect to an arbitrary rotation about the principal axis, here the z axis, the x and y axes may be chosen in such a manner as to simplify Eqs. (15). The most apt choice of the x and y axes is to let one, say the x axis, be perpendicular to the direction of propagation, i.e., to set $l=0$. With this choice of axes, and using the simplification imposed by the hexagonal symmetry, we reduce the set of Eqs. (15) to the following:

$$\{m^2(c_{11} - c_{12})/2 + n^2 c_{44} - \rho c^2\} \alpha = 0,$$

$$(m^2 c_{11} + n^2 c_{44} - \rho c^2) \beta + mn(c_{12} + c_{44}) \gamma = 0, \quad (16)$$

$$mn(c_{13} + c_{44}) \beta + (m^2 c_{44} + n^2 c_{33} - \rho c^2) \gamma = 0.$$

One solution is obvious, namely,

$$(\alpha_1, \beta_1, \gamma_1) = (1, 0, 0), \quad (17)$$

the correct value of c^2 , say c_1^2 , being given by

$$\rho c_1^2 = m^2(c_{11} - c_{12})/2 + n^2 c_{44}. \quad (18)$$

This solution represents a pure transverse wave with its vibration in the plane of symmetry.

Since the second and third solutions must be orthogonal to the first, they are of the form $(0, \beta, \gamma)$. These solutions must thus satisfy the two equations

$$(\lambda_{11} - \rho c^2) \gamma + \lambda_{12} \beta = 0, \quad \lambda_{12} \gamma + (\lambda_{22} - \rho c^2) \beta = 0,$$

⁶ Love, reference 5, p. 152.

where

$$\lambda_{11} = m^2 c_{44} + n^2 c_{33}, \quad \lambda_{12} = mn(c_{13} + c_{44}), \quad (19)$$

$$\lambda_{22} = m^2 c_{11} + n^2 c_{44}.$$

These equations were studied in the preceding section (cf. Eqs. (11)). Let us denote the two values of c^2 for which nontrivial solutions exist by c_2^2 and c_3^2 . These are then given by (13a) and (13b), respectively. The corresponding solutions are

$$(\alpha_2, \beta_2, \gamma_2) = (0, \sin \varphi, \cos \varphi), \quad (20)$$

$$(\alpha_3, \beta_3, \gamma_3) = (0, \cos \varphi, -\sin \varphi),$$

where φ is given by (14).

§4. NUMERICAL RESULTS FOR Zn AND Cd

Since $\mu(\mathbf{n})$ has rotational symmetry for metals with hexagonal symmetry, we need explicitly calculate $\mu(\mathbf{n})$ with respect to only two directions for Zn and Cd (see Eq. (3)). This involves merely the evaluation of the integral in (4). Each term with $j=1, 2$, or 3 refers to one type of wave, i.e., to one solution of Eqs. (15). Since the lattice of Zn and Cd is only slightly distorted from an ideal close packed arrangement, λ_0 was taken to be independent of \mathbf{n} . Further, the quantization factor $\Phi(x) + x/4$ was found to have a negligible effect at or above room temperatures. Hence the simplified formula (6) was used.

The velocities $c(1, n)$, $c(2, n)$, $c(3, n)$ have been calculated by Grüneisen and Goens⁷ by numerical

⁷ Grüneisen and Goens, *Zeits. f. Physik* **26**, 247 (1924), had occasion to calculate the wave velocities of the hexag-

onal crystals Zn and Cd. Not observing that Eqs. (15) can be reduced in these special cases, they resorted to a numerical solution, for each direction, of the cubic equation obtained from (15). Their cubic Eq. (4) contains in fact $q - c_{44}'$ (in their notation) as a factor.

TABLE II.

θ (in degrees)	10	20	30	40	50	60	70	80	90
φ (in degrees)									
Zn	35.5	45.6	52.0	58.1	64.8	71.0	77.3	83.8	90
Cd	18.4	33.6	45.5	55.4	64.0	70.3	77.0	83.8	90

The integration in (6) was performed numerically. Expressed in terms of M , Eq. (1), the final results are:

$$\text{Zn: } M = 1.1 \times 10^{-3} \{1.80 \cos^2 \theta + \sin^2 \theta\} \times T(\sin \theta / \lambda)^2,$$

$$\text{Cd: } M = 1.6 \times 10^{-3} \{1.73 \cos^2 \theta + \sin^2 \theta\} \times T(\sin \theta / \lambda)^2,$$

where θ is the angle between \mathbf{n} and the principal axis, and where λ is the wave-length of the incident x-rays expressed in Angstrom units.

onal crystals Zn and Cd. Not observing that Eqs. (15) can be reduced in these special cases, they resorted to a numerical solution, for each direction, of the cubic equation obtained from (15). Their cubic Eq. (4) contains in fact $q - c_{44}'$ (in their notation) as a factor.