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The Effect of Temperature on the Intensity of Reflection of X-Rays from Zinc Crystals

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Measurements have been made of the intensity of x-rays reflected from powdered zinc crystals at room temperature and at the temperature of liquid air. The atomic structure factors for the zinc atom at these temperatures are found to depend on the orientation of the particular plane from which the reflection of the x-rays takes place. Planes whose normals make small angles ψ with the c axis of the crystal give abnormally low values of the structure factor, while planes for which ψ is large give high values. From the measurements at the two temperatures the temperature factor for the various planes has been determined and with the aid of this factor the structure factor for the atom at rest has been calculated. The structure factor data for the atom at rest do not lie on a smooth curve as one might expect, but are also found to depend on the value of ψ. This indicates that the zinc atoms in the crystal do not possess spherical symmetry but are drawn out in the direction of the c axis. The average structure factor curve obtained experimentally has, however, been found to be in satisfactory agreement with a similar curve obtained from the theoretical charge distribution in the atom. The amplitude of thermal vibration of the atoms along various directions in the crystal has been determined. A comparison is made of the root mean square displacement as determined from the x-ray measurements with the average value obtained from specific heat data and a good agreement is found.

THE effect of temperature on the intensity of x-rays reflected from crystals has been studied by a number of investigators for the case of crystals of cubic symmetry. The theory for this case has been worked out by Debye and Waller and it has been found that the theory is in accord with experiment for temperatures up to about 400°Abs., above which the assumptions on which the theory is based are not valid.

In this paper a report is given of measurements of the intensity of reflection of x-rays from zinc crystals, how this depends on the temperature, and the conclusions which can be drawn from these measurements about the nature of the crystal and the atoms within the crystal.

In the case of zinc the Debye-Waller theory does not apply, since this theory was worked out for atoms of cubic symmetry. If zinc were an ordinary close packed hexagonal crystal, i.e., one having an axial ratio of 1.63, it is not unlikely that the Debye-Waller theory would have given an approximate explanation of the effect of temperature on the intensity of the reflected x-rays. However, zinc like cadmium differs considerably from the perfect close packed hexagonal structure in that the axial ratio is about 1.86 in place of the above-mentioned value. This value of the axial ratio means that the atoms are about 12 percent farther apart along the c axis than along a direction at right angles to this axis. This anisotropy of the crystal might lead one to expect that the amplitude of thermal vibration of the atoms is greater along the c axis than at right angles to it. One might also suppose that the atom itself is distorted, having a greater concentration of the outer electrons in one direction. If either or both of these effects are present, the measured values of the intensity of reflection of x-rays will be a function of the orientation with respect to the c axis of the particular plane which is reflecting the radiation, and in both cases the effect will be to decrease the intensity of reflection from planes whose normal makes a small angle with the c axis and increase the intensity for planes whose normal makes a large angle with this axis. Fortunately, however, any asymmetry of the atom will be noticed at small angles of scattering, while the effect of thermal vibration becomes larger as the angle of scattering increases.

A theoretical investigation of the effect of the anisotropy of the thermal vibrations on the intensity of reflection in zinc crystals has been

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made by Zener.[1] Measurements of the intensity of reflection of x-rays by zinc crystals at room temperature have already been made by Brindley,[2] while Jauncey and Bruce[3] have made measurements of the diffuse scattering of x-rays by zinc crystals. Both these experiments indicate that there is a considerable difference in the intensity of reflection from planes variously oriented with respect to the principal axis of the crystal.

However, only by measurements of the intensity of reflection at two or more temperatures can a quantitative relation between the intensity of reflection and the orientation of the reflecting planes be established, and it is primarily with this purpose in mind that this investigation has been carried out.

EXPERIMENTAL PROCEDURE

In this work the photographic method of recording the intensities has been used. With this method the powdered crystal sample to be studied can be in the form of a very thin cylinder or in the form of a plate. The method of the cylinder has been used successfully by a number of investigators, but when the material to be studied is of large atomic weight the corrections for absorption become rather uncertain. The method of reflecting the x-rays from a flat plate of the powder has been used by Brindley and Spiers[4] and by Brentano[5] and has been discussed by them. It has the advantage of permitting a simple calculation of the absorption correction to be made and also on account of the Bragg focusing effect sharp lines are obtained with a wide incident beam and hence the exposure time is much reduced. This latter method was used in this work.

The sample of finely powdered zinc was prepared by subliming the zinc in a vacuum and collecting the condensed vapor. This zinc powder was held in a circular copper disk in which a depression about 1.5 cm in diameter by 1.5 mm in depth was turned out. This disk was held accurately in the center of the camera in contact with the inside cylinder of a metal Dewar flask which constituted the top of the camera. The inside of the Dewar was made of a very thin walled brass tube on the bottom of which was silver soldered a copper rod, half of which was accurately milled away on the lower end to form the sample holder. The inside was drilled out to allow the liquid air to come to about 1/8 inch from the back of the sample. The temperature of the sample was found to come immeasurably close to the temperature of liquid air. The flat surface of the sample holder allowed an x-ray mark to be made along a narrow strip on the edge of the film from which the angular setting of the sample with respect to the primary beam could be determined. This method gave values which agreed very well with the readings of a scale marked on the outside of the camera. The camera was evacuated with an ordinary fore pump and one filling of liquid air usually sufficed for each picture.

MEASUREMENTS

From the microphotometer traces of the films the integrated intensity of reflections from the various planes was determined with the aid of intensity *vs.* blackening calibration marks on each film. A simple method of converting blackening into integrated intensities was used, and this will be described elsewhere. From the measured intensities one can determine the atomic structure factor with the aid of the well-known theory of reflection of x-rays from a flat plate of powder. In the notation used by Brindley the intensity I of the reflected x-rays is given by the expression

$$I=(\text{constant})pS^2f_T{}^2\phi(\theta)A, \qquad (1)$$

where f_T is the atomic structure factor at the temperature T, S is the crystal structure factor which in the case of zinc is equal to 1, 2 and $\sqrt{3}$ for different reflecting planes, p is the multiplicity factor, $\phi(\theta)=(1+\cos^2 2\theta)/(\sin\theta\sin 2\theta)$ and $A=\sin(2\theta-\alpha)/(\sin(2\theta-\alpha)+\sin\alpha)$, where α is the angle between the incident beam and the plane face of the reflecting powder. This factor A takes account of the absorption of the x-rays in the powder sample. Since several values of α are

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[1] C. Zener, Phys. Rev. **49**, 122 (1936).

[2] G. W. Brindley, Phil. Mag. **21**, 790 (1936).

[3] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 408 and 413 (1936).

[4] G. W. Brindley and F. W. Spiers, Proc. Phys. Soc. **46**, 841 (1934).

[5] J. C. M. Brentano, Proc. Phys. Soc. **47**, 932 (1935).

TABLE I. *Relative and absolute values of the structure factor at 295° Abs. and 85° Abs.*

				ROOM TEMPERATURE			LIQUID-AIR TEMPERATURE		
					rel.	Abs.		rel.	Abs.
Line	$\sin\theta/\lambda$	ψ^0	$pS^2\phi(\theta)$	I/A	f_{295}	f_{295}	I/A	f_{85}	f_{85}
0002	0.203	0	71.0	244	1.85	19.2	246	1.86	20.2
$10\bar{1}0$	0.217	90	45.3	223	2.22	23.0	218	2.20	22.8
$10\bar{1}1$	0.240	65.0	216.2	735	1.84	19.1	836	1.96	20.4
$10\bar{1}2$	0.297	47.0	43.0	111	1.61	16.6	119	1.67	17.4
$10\bar{1}3$	0.373	35.5	73.9	107	1.20	12.4			
				210	1.31	13.6	258	1.45	15.1
$11\bar{2}0$	0.376	90	48.3	103	1.46	15.1			
0004	0.405	0	13.8	13.7	1.00	10.3	22.0	1.26	13.1
$11\bar{2}2$	0.427	61.7	74.7	100	1.16	12.0	124	1.29	13.4
$20\bar{2}1$	0.446	76.9	52.5	78.2	1.22	12.6	92.0	1.32	13.7
$20\bar{2}3$	0.530	55.0	52.1	33.0	0.795	8.2	49.5	0.975	10.1
$10\bar{1}5$	0.551	23.2	56.6						
				52.3	0.630	6.5	96.0	0.850	8.8
$11\bar{2}4$	0.553	42.8	76.4						
$21\bar{3}1$	0.583	80.0	141.9	81.1	0.756	7.8	114	0.896	9.3
0006	0.608	0	20.4						
				30.0	0.608	6.3	49.0	0.765	8.0
$21\bar{3}2$	0.609	70.6	63.6						

used for each reflection it is convenient to tabulate the quantities I/A as representing the measured intensities. The experimental values of I/A are tabulated in the fifth column of Table I for the measurements at room temperature and in the eighth column of this table for the measurements at the temperature of liquid air. From these relative values of I/A relative values of f_T can be calculated with the aid of Eq. (1). In order that such values of the structure factor have any significance they must be put on an absolute basis. Since a direct evaluation of the absolute values is a difficult problem in itself it has become customary to accomplish the task by comparing the reflection from one or more planes of the substance under consideration with the reflections from some convenient planes of a crystal for which absolute measurements have already been made. This has been done with crystals of KCl and aluminum and Brindley has used these for standardizing the reflections from zinc. We have not repeated the work of Brindley in this respect but have accepted his absolute value for the reflection from the $11\bar{2}2$ plane as standard. He gives the experimental value of the structure factor for this plane and for copper $K\alpha$ radiation as 12.0. The absolute structure factors at room temperature which we obtain on the basis of this standard value are given in the sixth column of Table I.

In the case of some reflections two lines are unresolved and only the sum of the intensities is measured. In this case an average value of the structure factor $\bar{f}_T$ has been calculated. If the suffixes 1 and 2 indicate the two reflections, then the combined intensity is given by

$$I/A = \text{constant}\ [p_1S_1{}^2\phi_1(\theta)f_1{}^2 + p_2S_2{}^2\phi_2(\theta)f_2{}^2], \quad (2)$$

$$= \text{constant}\ [p_1S_1{}^2\phi_1(\theta) + p_2S_2{}^2\phi_2(\theta)]\bar{f}_T{}^2. \quad (3)$$

As is seen in what follows in the case of a crystal like zinc, it is generally not true that $f_1 = f_2 = \bar{f}_T$.

The relative values of the structure factor at liquid-air temperature are calculated in a similar manner as for room temperature from the measured values of I/A using Eq. (1). In order that these values can be compared with the absolute values at room temperature they must be standardized in terms of the room temperature data. This was accomplished in the following way. A sample containing a mixture of zinc powder and powdered magnesium oxide was used. Magnesium oxide has the advantage that it is readily obtainable in the form of a fine powder and also, due to its very high characteristic temperature, the effect of temperature on the intensity of reflection is very small. Any error which would be made in the calculation of its temperature factor from the values of the characteristic temperature are negligible. With this mixed sample, photographs were taken at room temperature and at the temperature of liquid air. The intensities of reflection for the 220 line of MgO were compared with those for the $10\bar{1}3$ and $11\bar{2}0$ pair for zinc. The result of this comparison gave the ratio of the intensity of the $10\bar{1}3$ and $11\bar{2}0$ pair at liquid-air temperature to the same pair at room temperature as 258/210 as indicated by the relative values of I/A for these lines in Table I. On the basis of this ratio of the intensities one obtains the following relation for the structure factor at the two temperatures.

$$[f(10\bar{1}3+11\bar{2}0)]_{T=85^\circ\text{K}}$$
$$=1.11[f(10\bar{1}3+11\bar{2}0)]_{T=295^\circ\text{K}}$$

and it is on the basis of this standardization that the absolute values of the structure factors for the temperature of liquid air are given in the last column in Table I.

Determination of the Temperature Factor

The atomic structure factor f_T which represents the amplitude of scattering by an atom in a crystal at temperature T is related to the structure factor f_0 for the atom at rest by the equation

$$f_T = f_0 e^{-M}, \tag{4}$$

where e^{-M} is commonly referred to as the Debye-Waller temperature factor. An expression for the exponent M was derived by Debye and Waller for the case of a cubic crystal of atoms of one kind and is given by the relation

$$M = \frac{6h^2T}{mk\Theta^2}\left(\phi(x)+\frac{x}{4}\right)\frac{\sin^2\theta}{\lambda^2}, \tag{5}$$

where m is the mass of the atom, Θ is the characteristic temperature of the crystal, $x=\Theta/T$ and $\phi(x)$ is the function which appears in the Debye theory of specific heats. The factor $(\phi(x)+x/4)$ which is referred to as the quantization factor does not differ much from unity when the temperature is larger than the characteristic temperature of the crystal. One sees then that for cubic crystals the exponent in the temperature factor is very nearly proportional to the temperature and to $\sin^2\theta/\lambda^2$.

Zener has investigated theoretically the effect of temperature on the intensity of reflection of x-rays from anisotropic crystals and gives an equation of the following form for the case of crystals like zinc or cadmium.

$$M = (a\cos^2\psi + b\sin^2\psi)\left(\phi(x)+\frac{x}{4}\right)\frac{\sin^2\theta}{\lambda^2}, \tag{6}$$

where a and b are constants and ψ is the angle which the normal to the reflecting plane makes with the c axis. If, as he indicated, a and b are linear functions of the temperature, we can factor out T and the equation can be written in the form

$$M = AT(B\cos^2\psi+1)Q(\sin^2\theta/\lambda^2), \tag{7}$$

where A and B are now constants independent of the temperature and Q has been written for the quantization factor which is, however, also a function of temperature, although its total effect is small.[6]

Since the intensity of reflection of x-rays is proportional to the square of the structure factor, we have from Eq. (4) that

$$I_1/I_2 = e^{-2(M_1-M_2)}, \tag{8}$$

where the subscripts 1 and 2 refer to the intensities and the temperature factors at two different temperatures. Hence we have

$$\log(I_2/I_1) = 2(M_1-M_2) \tag{9}$$

and substituting from Eq. (7) we can write

$$\begin{aligned}\frac{\log(I_2/I_1)}{(\sin\theta/\lambda)^2} &= 2A(T_1Q_1-T_2Q_2)(B\cos^2\psi+1)\\ &= 2AB(T_1Q_1-T_2Q_2)\cos^2\psi\\ &\quad +2A(T_1Q_1-T_2Q_2).\end{aligned} \tag{10}$$

Hence we see that a plot of the quantity on the left side of this equation against $\cos^2\psi$ will make it possible to evaluate the constants A and B from the slope and the intercept of the curve if it turns out to be a straight line.

In Table II, column 5 are given the values of I_2/I_1 for the ratio of the intensities at the temperature of liquid air and at room temperature for a number of suitable reflecting planes, and with the aid of the other data in Table II the curve of Fig. 1 is obtained. Unfortunately one is restricted in the range of values of $\cos^2\psi$ by the fact that some of the most desirable values occur for lines which cannot be resolved. The point on the curve corresponding to the largest value of $\cos^2\psi$ is taken for one of these pairs but in this case the angle ψ for both lines is small. There is, however, a considerable difference in the values of $\cos^2\psi$ for the two lines constituting this pair but it is not believed that a very large uncertainty in the slope of the curve is introduced by using the intensity ratio for these lines at an average value of $\cos^2\psi$. The 0004 line was not included in this graph because it is a weak reflection and the accuracy of its measurement was not considered as good as for the other lines.

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[6] It is likely that Q is also a function of the angle ψ, but since its total effect is small this refinement will be disregarded.

The slope of this curve has been taken equal to 1.57 and the intercept has been taken as 0.87. Room temperature was equal to 295° Abs. and the temperature of liquid air was 85° Abs. Taking the value of the characteristic temperature as determined by specific heat data $\Theta = 235$ as representing an average value for the crystal, one finds that the quantization factor is given by $Q = 1.018$ at 295° Abs. and 1.20 at 85° Abs. Using these data for evaluating the constants A and B we obtain the following values, $A = 2.2$ and $B = 1.8$. Substituting these values into Eq. (7), we obtain the experimentally determined temperature factor as

$$M = 2.2\times10^{-3}T(1.8\cos^2\psi + 1)Q(\sin^2\theta/\lambda^2). \quad (11)$$

The Atomic Structure Factor for the Zinc Atom at Rest

Using the value of M given by Eq. (11), the constants of which have been determined experimentally, we can now calculate the atomic structure factor for the atom at rest by using the relation $f_0 = f_T e^{M_T}$. The values of M_T and e^{M_T} for room temperature and for the temperature of liquid air are tabulated in Table III for all the lines measured. For the lines which are not resolved each member of the pair will have its particular temperature factor and it is then necessary to define an average value which can be applied to the average structure factor at the temperature at which it was measured. This has been done in the following way. If we assume that the structure factor for the two lines is the same for the atom at rest, we have, acccording to Eq. (1) that the total intensity of the pair is given by

$$I/A = \text{constant}\quad [P_1e^{-2M_1} + P_2e^{-2M_2}]f_0^2, \quad (12)$$

where P has been written in place of $pS^2\phi(\theta)$. We can also express this in terms of an average value of M by writing

$$I/A = \text{constant}\ [P_1 + P_2]e^{-2M_{\text{Av}}}\cdot f_0^2. \quad (13)$$

These equations can now be solved for $e^{M_{\text{Av}}}$ and we obtain

$$e^{M_{\text{Av}}} = \left[\frac{P_1 + P_2}{P_1e^{-2M_1} + P_2e^{-2M_2}}\right]^{\frac{1}{2}}. \quad (14)$$

The average values of the temperature factor which are listed in the table for the unresolved lines have been calculated in this way. A small error is introduced by calculating the averages in this way for lines having a small value of $\sin\theta/\lambda$ since, as we shall see, the structure factor for the atom at rest depends not only on $\sin\theta/\lambda$ but also to some extent on the value of ψ for the particular plane from which the reflection takes place. This will, however, only be appreciable for the first unresolved pair and since these have been resolved at room temperature, no appreciable inaccuracy will be introduced by this method of averaging.

Table II. *Ratio of intensities I_2/I_1 at 85° Abs. and 295° Abs.*

Line	$\frac{\sin^2\theta}{\lambda^2}$	ψ^0	$\cos^2\psi$	$\frac{I_2}{I_1}$	$\frac{\log(I_2/I_1)}{(\sin\theta/\lambda)^2}$
$11\bar{2}2$	0.182	61.7	0.224	1.24	1.18
$20\bar{2}1$	0.199	76.9	0.052	1.17	0.79
$20\bar{2}3$	0.280	55.0	0.328	1.49	1.42
$10\bar{1}5$ $11\bar{2}4$	0.305	23.2 42.8	0.690	1.82	1.97
$21\bar{3}1$	0.340	80.0	0.030	1.40	0.99

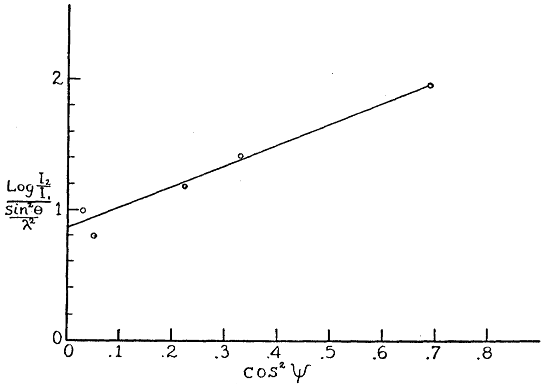

Fig. 1.

The values of the structure factor for the atom at rest which we have determined by the application of the temperature factor are listed in columns eight and nine of Table III. These values will differ from the true atomic structure factor for the atom at rest by an additive quantity Δf_0 which arises from the fact that the copper $K\alpha$ radiation used in these measurements lies close to and on the long wave-length side of the K critical absorption limit for zinc. This has the effect of changing the ordinate of the curve and need only be considered when a comparison with the theoretical values is made. For this reason, however, we have listed the values as f_0'.

A comparison of the f_0' values calculated from the room temperature data with those calculated from the measurements at the temperature of liquid air shows a satisfactory agreement, as should be expected. These values are also shown plotted together with the original values in Fig. 2. Since so many points are included in this figure, the average of the two sets of f_0' data have been replotted in Fig. 3. This shows very strikingly the fact that one does not get a single smooth structure factor curve for the atom at rest, as has been heretofore obtained with the isotropic crystals on which previous work has been done. The significance of this will be discussed below.

In order to make a comparison of the values of f_0' which we have obtained experimentally with those obtained from theory, we must take an average value of the experimental points, since the theoretical values are worked out for an isolated atom which lead to values lying on a smooth curve. The structure factors for the zinc atom have not as yet been calculated directly by the Hartree method of self-consistent fields but Brindley[2] has arrived at an f_0 curve for zinc which should be very approximately the same as that which one would obtain by a direct application of the Hartree method. The values which he obtains in this way for $f_0' \equiv f_0 - \Delta f_0$ where we take $\Delta f_0 = 2.2$ are shown in the first row of Table IV, and the corresponding values of f_0' which we have taken as representing a proper average of our experimental values are shown in the second row. The agreement between the theoretical and experimental values is as good as can be expected in view of uncertainties in the theoretical values as well as in the determination of the proper average experimental values.

THE ASYMMETRY OF THE ZINC ATOM

Let us return to a consideration of the atomic structure factors for the zinc atom at rest as plotted in Fig. 3. We have seen that the points do not fall on a single smooth curve but tend to separate as one goes to smaller values of sin θ/λ. Two limiting curves have been drawn in and it is apparent that the points having small values of ψ lie near the lower curve, those having large values of ψ lie near the upper curve, while points for which ψ has intermediate values lie in between. As was indicated in the introduction, this type of bifurcation, which becomes more pronounced toward small angles, is a definite indication that the zinc atom does not possess spherical symmetry.

From the nature of these data one is led to conclude that the electron atmosphere in a zinc atom is distorted so that the atom is more or less spheroidal in shape with the long axis directed along the c axis of the crystal. The rather large separation of the limiting curves at small values of sin θ/λ and the fact that this separation extends approximately to sin $\theta/\lambda = 0.6$ would indicate that several of the outer electrons in zinc are associated with the asymmetry.

THE AMPLITUDE OF THERMAL VIBRATION OF THE ZINC ATOMS

The exponent M of the temperature factor is related to the mean square amplitude of thermal vibration of the atoms normal to the plane from which the x-rays are reflected by the equation

$$M = 8\pi^2 u_\psi^2 (\sin\theta/\lambda)^2, \tag{15}$$

where u_ψ is the root mean square displacement of the atom in a direction which makes an angle ψ with the c axis of the crystal. This equation involves no assumption about the nature of the

TABLE III. *Temperature factor M and the structure factor f_0' for the atom at rest.*

LINE	$\frac{\sin^2\theta}{\lambda^2}$	$\cos^2\psi$	M_{295}	$e^{M_{295}}$	M_{85}	$e^{M_{85}}$	f_0'	
							$f_{295}e^{M_{295}}$	$f_{85}e^{M_{85}}$
0002	0.041	1.00	0.078	1.081	0.028	1.028	20.4	20.4
$10\bar{1}0$	0.047	0	0.031	1.031	0.011	1.011	23.6	23.0
$10\bar{1}1$	0.058	0.179	0.049	1.050	0.173	1.017	20.0	20.7
$10\bar{1}2$	0.088	0.466	0.107	1.116	0.038	1.039	18.5	18.1
$10\bar{1}3$	0.139	0.661	0.201	1.222	0.070	1.072	15.2	
				1.170		1.056	15.9	15.9
$11\bar{2}0$	0.141	0	0.092	1.096	0.033	1.034	16.5	
0004	0.164	1.00	0.313	1.368	0.111	1.117	14.1	14.6
$11\bar{2}2$	0.182	0.224	0.169	1.184	0.059	1.061	14.2	14.2
$20\bar{2}1$	0.199	0.052	0.145	1.156	0.052	1.053	14.5	14.4
$20\bar{2}3$	0.281	0.328	0.297	1.345	0.108	1.114	11.0	11.2
$10\bar{1}5$	0.304	0.842	0.503	1.655	0.178	1.195		
				1.55		1.17	10.1	10.3
$11\bar{2}4$	0.306	0.539	0.396	1.486	0.141	1.152		
$21\bar{3}1$	0.340	0.030	0.236	1.266	0.083	1.087	9.9	10.1
0006	0.370	1.00	0.680	1.97	0.240	1.272		
				1.43		1.13	9.0	9.0
$21\bar{3}2$	0.370	0.111	0.294	1.34	0.103	1.109		

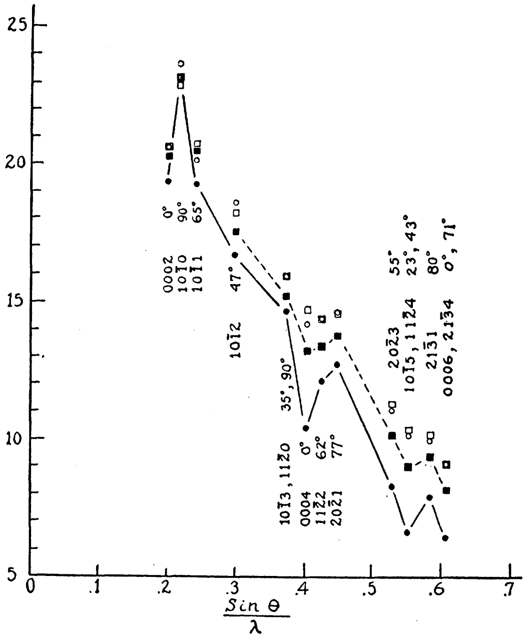

FIG. 2. The solid circles represent values of the structure factor as measured at room temperature, the solid squares represent the values at liquid-air temperature, while the open circles and squares represent the same quantities when respectively reduced to the atom at rest by means of the measured temperature factors. The values of the angles ψ in round numbers and the indices have been written in for each line. For the points at $\sin\theta/\lambda=0.3$ the average value is given for both temperatures, although this line was resolved at room temperature.

vibrations. Hence with the aid of this equation and the experimentally determined relation for M, one can solve for u^2_ψ, obtaining

$$u^2_\psi=\frac{M}{8\pi^2(\sin\theta/\lambda)^2}=\frac{2.2\times T\times 10^{-3}}{8\pi^2}\times[1.8\cos^2\psi+1]Q. \quad (16)$$

Using this equation, we can now calculate the root mean square displacement of the atoms at any temperature T and along any direction in the crystal. When $\psi=0$, i.e., for vibrations parallel to the c axis of the crystal, we find at room temperature that $u_{\psi=0}=0.153$A. Likewise in a direction perpendicular to the c axis we find that $u_{\psi=90}=0.0913$A. We can similarly calculate this quantity for intermediate values of ψ and we then obtain the root mean square vibration as a function of the direction in the crystal, as shown graphically in Fig. 4.

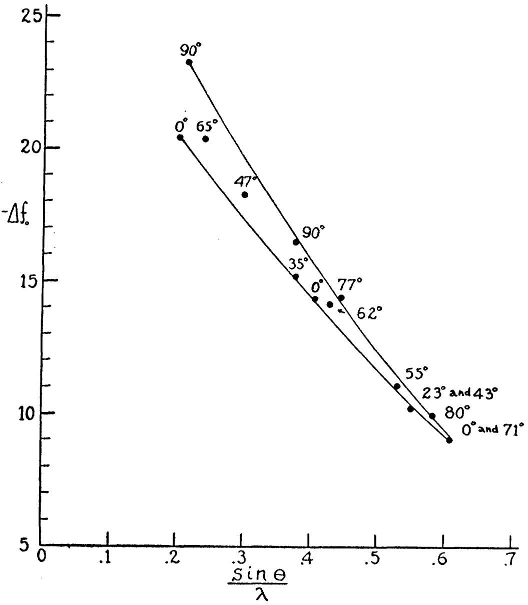

FIG. 3. This curve represents the average structure factor for the atom at rest less the dispersion correction. The two curves have been drawn in to indicate the effect of the asymmetry of the zinc atom.

THE CHARACTERISTIC TEMPERATURE OF ZINC

We have seen how the x-ray measurements lead to information about the atomic vibrations along the various directions in a zinc crystal. From measurements of the specific heat one also obtains information about the atomic vibrations, but in this case only an average value can be determined. It is of interest to compare the results from these two sources. Let us assume that the Debye-Waller theory gives an average value of the temperature factor for the zinc crystal. We can then combine Eq. (15) and Eq. (5) to get an average value of the mean square vibrations of the atoms in the crystal, and this gives

$$u^2=(3h^2T/4\pi^2mk\Theta^2)\cdot Q. \quad (17)$$

On solving this equation for Θ and substituting in the values of the constants for room tem-

TABLE IV. *Values of $f_0-\Delta f_0$, calculated and experimental.*

$\sin\theta/\lambda$	0.2	0.3	0.4	0.5	0.6
Theoretical Brindley	21.5	17.7	13.3	11.2	9.5
Average experimental	22.0	18.0	14.6	11.8	9.2

perature, we obtain

$$\Theta = \frac{260 \times 10^{-8}}{u}. \tag{18}$$

The value of Θ which we can calculate from this equation using an average experimental value of u can now be compared with the value of Θ obtained from measurements of the specific heat of zinc. Averaging the root mean square displacements over all values of ψ, one obtains the relation

$$u_{\mathrm{Av}} = \frac{u_{\psi=0} + 2u_{\psi=90}}{3} \tag{19}$$

and on substituting the numerical values at room temperature into this equation, we obtain $u_{\mathrm{Av}} = 0.112$A which average value is shown by the solid line in Fig. 4. This value when substituted into Eq. (18) gives us an average value of the characteristic temperature $\Theta_{\mathrm{Av}} = 232°$ Abs. The commonly accepted value obtained from specific heat measurements is $\Theta = 235°$ Abs. and one sees that the agreement is good beyond all expectation.

It is also possible on the basis of Eq. (18) to define two other characteristic temperatures for a zinc crystal corresponding to vibrations along the principal axis and perpendicular to it. If we had a crystal in which the root mean square vibrations had the value $u_{\psi=0} = 0.153$A the characteristic temperature of this crystal as determined by Eq. (18) would be $\Theta_{||} = 170°$ Abs. and likewise if the value $u_{\psi=90} = 0.0913$A were taken as the root mean square displacement, we would obtain a characteristic temperature $\Theta_{\perp} = 285°$ Abs. By defining two characteristic temperatures for the crystal in this way we have not given the quantity any vector properties, but have merely associated two values with the two directions in the crystal.

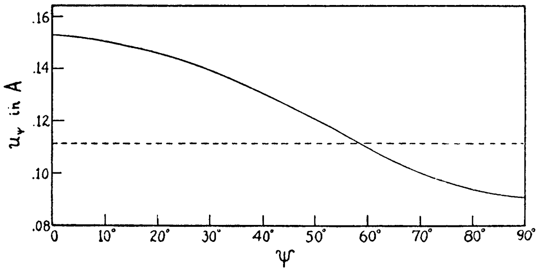

FIG. 4. The curve represents the dependence of thermal vibration on the direction in the crystal at room temperature. The value obtained from specific heat data is represented by the dotted line. This line also represents the measured values of u averaged over all values of ψ as accurately as it can be drawn on the curve.

One might stop here, but it should be pointed out that Grüneisen and Goens[7] in their measurements of the thermal expansion of zinc also obtain two values of the characteristic temperature along the two directions in the crystal. They give $\Theta_{||} = 200°$ Abs. and $\Theta_{\perp} = 320°$ Abs., values which are decidedly not in agreement with the results which we obtain, and at present no reason for this apparent discrepancy can be given.

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[7] E. Grüneisen and E. Goens, Zeits. f. Physik **29**, 141 (1924).