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Anisotropy in the Atomic Vibrations of Zinc Crystals

I. Evidence from X-Ray Scattering

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The results of Brindley's recent experiments on the intensity of the various reflections of Cu $K\alpha$ x-rays from powdered zinc crystals are compared with the results of the measurements made by the authors on the diffuse scattering of x-rays from single zinc crystals. When the method of diffuse scattering is used it is possible to obtain S values for various orientations of the crystal for a given value of $(\sin \frac{1}{2}\phi)/\lambda$. The form of Zener's formula for M for hexagonal crystals is confirmed by our experimental results. We find the root-mean-square thermal displacements of the atoms to be 0.172 and 0.093A, respectively, along and perpendicular to the c axis. These are greater than Brindley's values. They nearly explain the large difference between the F values for the (0002) and (10$\bar{1}$0) reflections. These two reflections possibly give some evidence of asymmetry in the electron structure of the zinc atoms, the structure being more diffuse in the direction of the c axis than normal to this direction.

1. POWDERED CRYSTAL METHOD

In November 1935 Brindley and Spiers[1] reported some very interesting results for the scattering of Cu $K\alpha$ x-rays ($\lambda=1.54$A) from powdered zinc. Since the Cu $K\alpha$ line is on the long wave-length side of the zinc K absorption edge ($\lambda=1.28$A), the zinc K fluorescence radiation is not excited. However, the wave-length 1.54A is sufficiently close to 1.28A to necessitate correction for dispersion. From their experimental results, Brindley and Spiers first calculated the F values[2] and from these they in turn calculated the f values[2] from the relation

$$f=Fe^{M}, \tag{1}$$

where e^{M} is the Debye-Waller temperature factor. Assuming a single characteristic temperature and using Waller's formula[3] for M, they obtained f values respectively for the (20$\bar{2}$1) and the (10$\bar{1}$5)+(11$\bar{2}$4) reflections[4] which do not fall upon a smooth curve. The importance of this fact was recognized by Brindley and Spiers. Brindley[5] has since obtained other reflections showing a similar peculiarity. Brindley and Spiers' experimental F values are shown as black circles in Fig. 1 and Brindley's later experimental F values are shown as crosses in the same figure.

2. THEORY

In January 1936 Zener[6] published the results of a theoretical investigation of the thermal vibrations of the atoms of an anisotropic crystal. Zener found that for hexagonal crystals the Debye-Waller M should be of the form

$$M=(a\cos^2\psi+b\sin^2\psi)\cdot(\sin^2\theta/\lambda^2), \tag{2}$$

where ψ is the angle between the c axis of a crystal and the normal to a reflecting plane of atoms in the crystal. The values for a and b were calculated for room temperature from the known elastic constants, the simple Debye model of a solid being used. These values are shown in the first row of Table I. Independently Brindley[7] has pointed out that according to Grüneisen and Goens two "characteristic temperatures" must be recognized for zinc—one for vibrations along the c axis and the other for vibrations normal to this axis. These different characteristic temperatures are accompanied by different M's in the two directions. Brindley[5] returns to this matter in a later paper and, using Zener's formula (2), gives the values for a and b shown in the second row of Table I.

The angle ψ is related to the Miller indices $(h, k, -h-k, l)$ by[5]

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[1] G. W. Brindley and F. W. Spiers, Phil. Mag. **20**, 865 (1935).

[2] Throughout this and subsequent articles we shall use F to indicate the atomic structure factor as modified by the thermal vibrations of the atom, and f to indicate the atomic structure factor for an atom at rest.

[3] I. Waller, Zeits. f. Physik **51**, 213 (1923). See also C. Zener and G. E. M. Jauncey, Phys. Rev. **49**, 17 (1936).

[4] Zinc is a hexagonal crystal and four Miller indices are used, the third index being the negative sum of the first two. The fourth index refers to the long or c axis.

[5] G. W. Brindley, Phil. Mag. **21**, 760 (1936).

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

[7] G. W. Brindley, Nature **137**, 315 (1936).

$$\cos\psi = (l/C)\{4(h^2+hk+l^2)/3+(l/C)^2\}^{-\frac{1}{2}}, \qquad (3)$$

where C is the axial ratio 1.856. From (1), (2) and (3), the f values for zinc can be calculated from Brindley's experimental F values. Brindley's F values for the $(20\bar{2}3)$, $(10\bar{1}5)+(11\bar{2}4)$, $(21\bar{3}1)$, and the $(0006)+(21\bar{3}2)$ reflections are most interesting since they give a zig-zag in Fig. 1. Unless $a>b$ in (2) the corresponding f values show a similar zig-zag. Brindley finds that the values of a and b shown in the second row of Fig. 1 smooth out the zig-zag better than do Zener's values shown in the first row. Now $(a-b)$ may be taken as a measure of the anisotropy of the atomic vibrations. Brindley's experimental results and also his theory based upon Grüneisen and Goens' idea of two "characteristic temperatures" thus indicate a much greater anisotropy $(a-b=0.785)$ than does Zener's original theory $(a-b=0.33)$. Accordingly, Zener[8] has looked into the theory again and has used a modified Debye model of a solid in which the discrete structure of the solid is taken into account. Zener's new values of a and b are shown in the third row of Table I. Although Zener's value of b agrees fairly well with Brindley's value, Zener's anisotropy $(a-b=0.465)$ is still too small to agree with experiment.

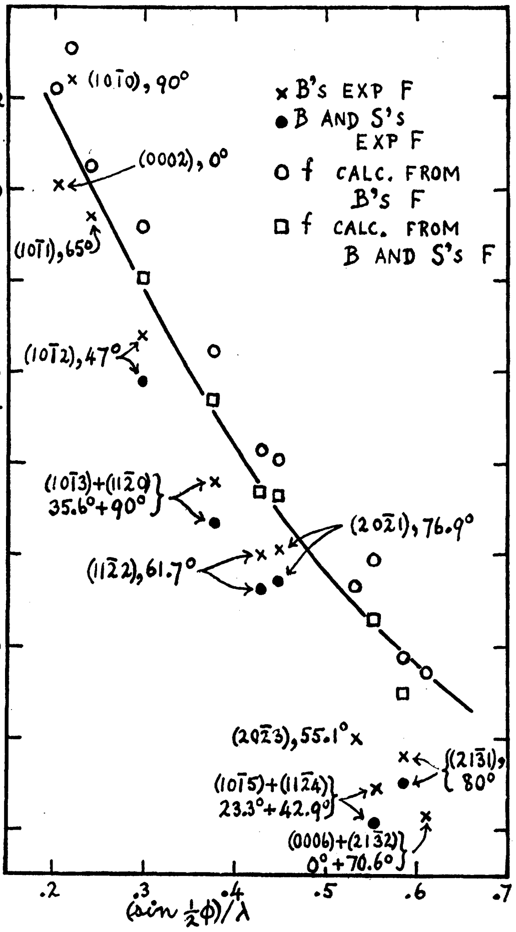

FIG. 1. Brindley's and Brindley and Spiers' experimental F values for zinc. Also these same values corrected for thermal vibration of the atoms, our values of a and b being used.

Now, although Brindley's f values for the reflections mentioned in the previous paragraph fall fairly well on a smooth curve, his f values for other reflections do not fall so well on this curve.[9] But more important still are what Brindley calls the anomalous f values for the (0002) and $(10\bar{1}0)$ reflections. The points representing these values distinctly depart from a smooth curve. Brindley suggests that the high F value for the $(10\bar{1}0)$ reflection may be due to an impurity. However, Brindley[10] finds the same kind of anomalous F values for these same reflections from cadmium. Hence the present authors infer that the F values for the (0002) and the $(10\bar{1}0)$ reflections indicate a much greater anisotropy than does Brindley's value, $a-b=0.785$. Evidence in support of this inference is given in the next section.

TABLE I. *Anisotropy of atomic vibrations. Zinc at 298°K.*

	a	b
Simple Debye Model	$0.75A^2$	$0.42A^2$
Brindley	1.295	0.51
Modified Debye Model	1.06	0.595
Jauncey and Bruce	2.34	0.68

3. DIFFUSE SCATTERING FROM SINGLE CRYSTALS

The theory of diffuse scattering of x-rays[11] from a crystal gives

$$S = S_{\mathrm{coh}} + S_{\mathrm{inc}}/(1+\alpha \operatorname{vers} \phi)^3, \qquad (4)$$

where

$$S_{\mathrm{coh}} = (f^2 - F^2)/Z \qquad (5)$$

and where, the extra negative term being

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[8] C. Zener, letter appearing in this issue of Phys. Rev.

[9] The reader is referred to the original paper.

[10] G. W. Brindley, Proc. Leeds Phil. Soc. 3, 200 (1936).

[11] See G. E. M. Jauncey and J. H. Deming, Phys. Rev. **48**, 577 (1935) for previous references.

neglected since its values are unknown but small for zinc,

$$S_{\mathrm{inc}} = 1 - (1/Z)\Sigma E_r^2. \tag{6}$$

Now imagine an atom removed from the crystal lattice without changing the structure of the electron atmosphere surrounding the nucleus. The scattering from such an atom is given by (4) but with (5) replaced by

$$S_{\mathrm{coh}} = f^2/Z. \tag{7}$$

Let S_{cryst} refer to S for a crystal and S_{atom} to an atom removed from the crystal. Then, from (4), (5) and (7),

$$S_{\mathrm{atom}} = S_{\mathrm{cryst}} + F^2/Z. \tag{8}$$

This is an interesting variation of the relation between S_{gas} and S_{cryst} announced by Jauncey and Harvey[12] several years ago. The two terms on the right of (8) may be considered as experimental quantities. The method of measurement of S_{cryst} has been described in various papers by Jauncey[11] and the measurement of F^2/Z for zinc crystals has been described by Brindley. For anisotropic crystals, both S_{cryst} and F^2/Z are functions of $(\sin \frac{1}{2}\phi)/\lambda$, where ϕ is the angle of scattering, and of ψ. Hence experimental values of S_{atom} for zinc can be found if, in addition to the powdered crystal measurements made on zinc, measurements of the diffuse scattering from single zinc crystals are also made. The S_{atom} values obtained from (8) will be a function of $(\sin \frac{1}{2}\phi)/\lambda$ and possibly of ψ. If they are a function of ψ, asymmetry in the electron structure of the zinc atoms will be indicated. *Eq. (8) brings out very forcibly the value of measurements on the diffuse scattering in problems such as that under discussion.*

For (8) to be directly applicable it would be necessary to use monochromatic rays in the diffuse scattering experiments. Although experiments are now being made in this laboratory with Mo $K\alpha$ rays scattered from rocksalt, yet the intensity of the diffusely scattered rays is very weak. To attempt to use Mo $K\alpha$ rays with zinc crystals was out of the question on account of the high absorption coefficient of zinc. We therefore used the general radiation from a tungsten tube. By the method of integration over the wave-lengths present in the spectrum as described by Jauncey and Claus[13] it is possible to compare theory with experiment provided that the theoretical values are known. However, it is a matter of experience that one can use an average wave-length as obtained from half-value absorption of the primary rays in aluminum and obtain reasonably correct S values. For the present we shall use this average wave-length as if it were the wave-length of monochromatic rays. In our experiments this wave-length was 0.435A. This excites the K fluorescence rays from zinc and it was necessary to place a sufficient thickness of aluminum before the ionization chamber window in order to reduce the fluorescence rays to a negligible intensity. Owing to the high absorption in zinc we could not use the method of transmission through a thin crystal. Instead we used the method of scattering from the front surface of the crystal specimens.

It is important to note that in diffuse scattering a new definition of the angle ψ is needed. It is the angle that the line bisecting the angle between the forward direction of the scattered rays and the backward direction of the primary rays makes with the c axis of the specimen. In diffuse scattering numerous values of ψ can be obtained for the same value of $(\sin \frac{1}{2}\phi)/\lambda$. As we shall describe the experimental details in a later paper, we now proceed to the results.

Having grown several single crystals of zinc, we were able to obtain the diffuse scattering at $\phi = 30°$ for various values of ψ ranging from 0° to 90°. The S values are shown as crosses in Fig. 2. These are all for $(\sin \frac{1}{2}\phi)/\lambda = 0.6$. We note the high S values for all values of ψ and the large difference between the S value for $\psi = 0°$ and that for $\psi = 90°$.

If there is asymmetry in the electron structure of zinc atoms it will be due to the valence electrons. At $(\sin \frac{1}{2}\phi)/\lambda = 0.6$ the contributions of these electrons to the f values may be neglected and so f and also ΣE_r^2 may be considered as independent of ψ. Now (2) may be written in the form

$$M = \{b + (a-b)\cos^2\psi\}(\sin^2 \tfrac{1}{2}\phi)/\lambda^2 \tag{9}$$

and so, from (1), (2), (4) and (5), we have at

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[12] G. E. M. Jauncey and G. G. Harvey, Phys. Rev. **38**, 1071 (1931).

[13] G. E. M. Jauncey and W. D. Claus, Phys. Rev. **46**, 941 (1934).

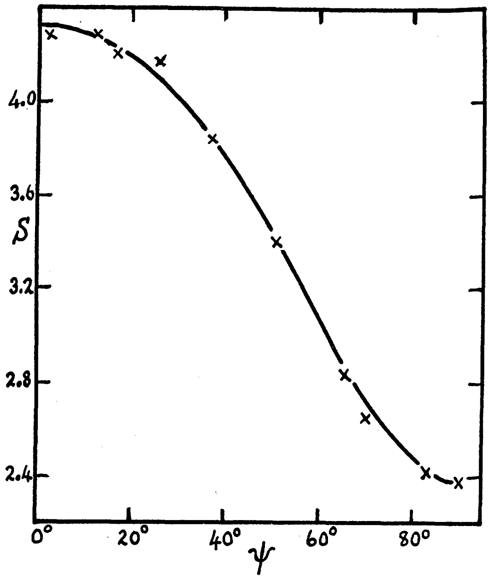

FIG. 2. Diffuse scattering of $\lambda=0.435$A from single crystals of zinc at $\phi=30°$ but for the orientation angle ψ varying from 0° to 90°.

$$(\sin\tfrac{1}{2}\phi)/\lambda=0.6$$

$$S_\psi=\text{const}-(F_{90°}^2/Z)\exp\left[-2(a-b)(\cos^2\psi\sin^2\tfrac{1}{2}\phi)/\lambda^2\right]. \quad (10)$$

For convenience we here introduce two notations: $F(10\bar{1}0)$ and $f(10\bar{1}0)$ are the F and f values for the $(10\bar{1}0)$ reflection, respectively, while $F(0.218, 90°)$ and $f(0.218, 90°)$ are the F and f values for $(\sin\frac{1}{2}\phi)/\lambda=0.218$ and $\psi=90°$. From Fig. 1, Brindley's most recent experimental value of $F(0.585, 80°)$ is 7.6. Now, from the form of (2), $M(80°)$ must nearly be equal to $M(90°)$ and so from the trend of the curve in Fig. 1 we estimate $F(0.6, 90°)=7.5$. But this last F is for Cu $K\alpha$ rays and contains the effect of dispersion. From data given on p. 806 of Brindley's paper,[5] this value must be multiplied by $11.7/(11.7-2.14)$ in order to obtain the F value for $\lambda=0.435$A, which is fairly far on the short wave-length side of the K absorption edge for zinc. This new value is 9.2 and is the value used for $F_{90°}$ in (10). From (10)

$$S_{0°}-S_{90°}=(F_{90°}^2/Z)\cdot\left(1-\exp\left[-2(a-b)\cdot(\sin^2\tfrac{1}{2}\phi)/\lambda^2\right]\right). \quad (11)$$

Our experimental value of $S_{0°}-S_{90°}$ is 1.94, so that upon solving (11) for $(a-b)$ we obtain 1.61. This amount of anisotropy is greater than that given by Brindley and much greater than the later value given by Zener. Putting this value of $(a-b)$ in (10) and using an arbitrary constant, we have plotted the curve shown in Fig. 2. The very good agreement between the experimental points and the curve shows the excellence of Zener's formula (2) and also of the method of diffuse scattering. Moreover, the agreement gives us some confidence in the value, $a-b=1.61$. Diffuse scattering experiments which do not involve the use of Brindley's experimental results and in which the method of integration over all wave-lengths in the spectrum of the primary rays is used give $a-b=1.66$ in reasonably good agreement with $a-b=1.61$. We shall take the higher value to be the more reliable. Further, these diffuse scattering experiments, which will be reported later, also give $b=0.68$ and therefore $a=2.34$. These values are shown in the fourth row of Table I.

Since[3] $$M=8\pi^2\overline{u_\psi^2}(\sin^2\tfrac{1}{2}\phi)/\lambda^2, \quad (12)$$

where $\overline{u_\psi^2}$ is the mean square displacement of an atom due to its thermal vibrations, we find from (2) that

$$(\overline{u_\psi^2})^{\frac{1}{2}}=\{(a\cos^2\psi+b\sin^2\psi)/8\pi^2\}^{\frac{1}{2}}. \quad (13)$$

Hence our results give

ψ	$(\overline{u_\psi^2})^{\frac{1}{2}}$
0°	0.172A
90°	0.093A

at room temperature. It is probably a coincidence that the ratio of these root-mean-square displacements very nearly equals the axial ratio.

Using the values of a and b shown in the fourth row of Table I we have calculated f values from Brindley's experimental F values. These f values are shown as white circles in Fig. 1. The curve in the figure is the quantum-mechanical f curve for zinc atoms estimated by Brindley[5] and corrected for dispersion. It is remarkable that the points for $f(20\bar{2}3)$, $f(21\bar{3}1)$, and $f(0006)+f(21\bar{3}2)$ fall so closely to the theoretical f curve. The point for $f(10\bar{1}5)+f(11\bar{2}4)$, however, departs considerably from the curve. But, if we use Brindley and Spiers' F value as represented by the black circle, we obtain an f point, represented by a white square, which does fall upon the theoretical curve. We feel therefore that there is good evidence for all these four f points falling upon the theoretical f curve. This is very satisfactory because at reasonably high values of $(\sin \frac{1}{2}\phi)/\lambda$, such as 0.532 to 0.610, the outer electrons contribute a negligible amount to f and the calculated theoretical f values are therefore more reliable. We note that at lower values of $(\sin \frac{1}{2}\phi)/\lambda$ the f points calculated from Brindley's F values fall above the curve. However, the f points calculated from Brindley and Spiers' values and represented by white squares tend to fall upon the theoretical curve. On the whole we believe that there is good evidence that all the f points fall close to the theoretical curve but with some tendency for the f points to be above the curve at small values of $(\sin \frac{1}{2}\phi)/\lambda$. It is in this region of $(\sin \frac{1}{2}\phi)/\lambda$ that the calculated theoretical f values become somewhat unreliable due to the contributions of the outer electrons. Considering errors of experiment and of theoretical calculation, the agreement is satisfactory with the notable exception of the point for $f(10\bar{1}0)$.

4. ASYMMETRY IN THE ELECTRON STRUCTURE?

From (1) and (2)

$$f(0002)/f(10\bar{1}0) = (F(0002)/F(10\bar{1}0))e^{0.0413(a-1.15b)}, \quad (14)$$

since $(\sin \frac{1}{2}\phi)/\lambda$ has the values 0.203 and 0.218 for the (0002) and $(10\bar{1}0)$ reflections, respectively. Using our values of a and b and Brindley's $F(0002)$ and $F(10\bar{1}0)$ values for Cu $K\alpha$ rays, we thus obtain

$$f(0002)/f(10\bar{1}0) = 0.958. \quad (15)$$

From the trend of the curve in Fig. 1, we estimate that

$$f(0.203,\ 90°) = 1.015f(0.218,\ 90°).$$

Hence

$$f(0.203,\ 0°)/f(0.203,\ 90°) = 0.958/1.015 = 0.944. \quad (16)$$

For simplicity we shall assume that this ratio also holds for $(\sin \frac{1}{2}\phi)/\lambda = 0.2$. According to p. 806 of Brindley's paper $f(0.2)$ for symmetrical zinc atoms is $23.7-2.14=21.6$ (say). We shall suppose that this is an average of $f(0.2,\ 0°)$ and $f(0.2,\ 90°)$, so that (16) gives $f(0.2,\ 0°)=21.0$ and $f(0.2,\ 90°)=22.2$. Although we place no great confidence in these f values, they indicate that $f(0.2,\ 0°)$ is somewhat less than $f(0.2,\ 90°)$ and so suggest the existence of some asymmetry in the electron structure of the zinc atoms. It is interesting to note that the asymmetry is such that the electron atmosphere is more diffuse in the direction of the c axis than in a direction normal to this axis.[14] It is the (0002) and $(10\bar{1}0)$ reflections which, because $(\sin \frac{1}{2}\phi)/\lambda$ is small and the values of ψ differ by the maximum amount, give the best chance of showing asymmetry in the electron structure. These reflections should be investigated further. The (0004) and $(20\bar{2}0)$ reflections should also prove of interest if they can be obtained unmixed with other reflections. The intensity of the (0004) reflection should prove to be low.

If there is asymmetry in the electron structure, it will be found that the f values obtained by correcting the F values for thermal vibrations will depart slightly from a smooth curve. The points will fall between two curves,[15] one for $\psi=0°$ and the other for $\psi=90°$. These curves will separate from each other at small values of $(\sin \frac{1}{2}\phi)/\lambda$.

5. CONCLUSION

We conclude that the experiments on diffuse scattering together with those on powdered crystals of zinc prove that the anisotropy of the thermal vibrations is much more than previously suspected. The anisotropy is almost sufficient to explain the anomalous F values obtained for the (0002) and $(10\bar{1}0)$ reflections. However, we hold the tentative opinion that these reflections indicate some asymmetry in the electron structure of the atoms of a zinc crystal.

We wish to thank Professor E. P. T. Tyndall and Mr. D. O. Holland of the State University of Iowa for valuable information in regard to the growing of zinc crystals.

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[14] The difference between $f(0.2,\ 90°)$ and $f(0.2,\ 0°)$ is 1.2. If this is due to the two valence electrons, then for each such electron $E(0.2,\ 90°)-E(0.2,\ 0°)=0.6$. The electron structure factor for each valence electron is probably somewhat like that for the electron in the hydrogen atom. For this latter electron $E(0.2)=0.5$ approximately. Taking this as the average of $E(0.2,\ 90°)$ and $E(0.2,\ 0°)$ we obtain $E(0.2,\ 90°)=0.8$ and $E(0.2,\ 0°)=0.2$. These are possible values.

[15] *Note added in proof:* In paper III of this series, Miller and Foster find evidence for $F(10\bar{1}1)=20.1$ for Cu $K\alpha$ rays. Using our values of a and b, we calculate $f(10\bar{1}1)=21.3$ for Cu $K\alpha$ rays. Referring to Fig. 1, we see that this f point falls between the curves which may be imagined as respectively passing through the f points for the (0002) and $(10\bar{1}0)$ reflections. Miller and Foster also confirm the value of $F(0002)/F(10\bar{1}0)$ found by Brindley.