ratio. Next we determined the ratio for an untreated crystal and obtained the value 1.62. These two values are equal within the experimental error even though the numerator and denominator of the ratio in the first case were about 10 percent larger than the numerator and denominator, respectively, in the second case. Similarly, we measured the ratio for two 0° crystals and obtained ratios of 1.66 and 1.68 for the treated and untreated crystals, respectively. Again, the ratios are equal within experimental error. By reference to Fig. 1, it is seen that the surface irregularities should produce no effect on the ratio of the scattering at two different temperatures. If the process of polishing, annealing and etching had produced distortion in the crystal lattice, it is likely that there would have been lack of agreement in the above ratios.

As a matter of interest we show two curves of $I(\phi, \theta)/u(\phi, \theta)$ (see a previous paper[3]) against θ for $\phi=30°$ and $\psi=0°$ in Fig. 2. The dotted curve is for $T=100°$K and the full curve is for $T=298°$K. It is seen that with increase of temperature the intensity of the Laue spot diminishes while the intensity of the diffuse scattering increases.

Our results are shown in Table I and in Fig. 3.

We now draw a horizontal line AB in Fig. 3. The ordinates of the points A and B indicate equal values of $(S\rho/\mu)_{\text{exp}}$. The temperature coordinates of these two points are 106° and 314°K. From (17) the value of a/b is therefore 2.96. This is the ratio of the mean square displacement in the direction of the c axis to that in a direction normal to this axis. It may be noted that this is considerably greater than the theoretical value 1.8 derived by Zener[1] from the elastic constants.

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Atomic Structure and Vibrations in Zinc Crystals

V. The Diffuse Scattering of X-Rays at Various Scattering Angles

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Former experimental results on the diffuse scattering of x-rays from single crystals of zinc at room temperature were not accurate enough to give certain evidence for the existence of asymmetry in the electron atmospheres of the zinc atoms. More exact and careful measurements of the diffuse scattering of x-rays at scattering angles ranging from $\phi=15°$ to $\phi=40°$ for the two orientation angles $\psi=14°$ and $\psi=90°$ are described. The results are discussed in paper VI.

1. INTRODUCTION

A RECENT experiment was performed in this laboratory[1] in which the diffuse scattering from single crystals of zinc was measured at values of ϕ, the angle of scattering, equal to 20°, 25°, 30°, 35°, and 40°. These results implied that the true atomic structure factor, f, is a function of ψ as well as $(\sin \frac{1}{2}\phi)/\lambda$. This must be due to asymmetry in the electron atmosphere of an atom in a zinc crystal. The data were not complete enough to make quantitative measurements of this asymmetry of the atomic structure factor.

2. EXPERIMENTAL REFINEMENTS

In the present experiment the diffuse scattering was measured at the same angles as before and also at $\phi=15°$. All of the measurements were made at room temperature. The expression for the experimental values is

$$(S\rho/\mu)_{\text{exp}}=\frac{4R^2Wm^2c^4}{ANZe^4(1+\cos^2\phi)}\cdot\frac{D(\phi,\theta)}{D_0u(\phi,\theta)}, \tag{1}$$

where $D(\phi, \theta)$, D_0 are the measured ionization currents[2] for the scattered and primary beams,

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

[2] For definition of terms and previous references, see G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 408 (1936).

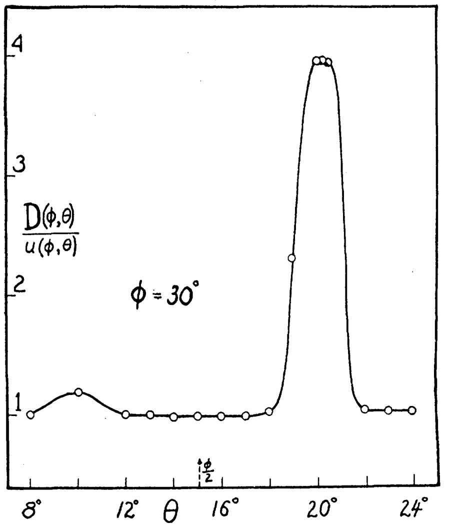

FIG. 1. Method of eliminating the Laue spot at $\theta=\phi/2$.

respectively, and

$$u(\phi,\,\theta)=\frac{2\sin(\phi-\theta)}{\sin(\phi-\theta)+\sin\theta}. \qquad (2)$$

In an experiment where the angle of scattering is varied, the effects of surface pitting described in the fourth paper[3] of this series are particularly important, as is seen by reference to Fig. 1 of the fourth paper. Thus it is essential to have no irregularities more than 10^{-5} cm deep. A polished and annealed surface was used for $\psi=90°$ and a cleaved surface for $\psi=14°$.

The quantity given in (2) is very sensitive to changes of θ for small values of ϕ. Hence each experiment was done with the ionization chamber and crystal first on one side and then the other side of the primary beam. Thus small errors in lining up the crystal in its holder were eliminated.

For accurate work it is best to observe the scattering at $\phi/2=\theta$ or to observe it at symmetrical positions about the angle $\phi/2=\theta$ and interpolate for the point $\phi/2=\theta$. With the cleaved surface crystal this latter method is always used, but, where the polished face of a moulded casting is used, the Laue spot may, in general, occur at any angle. However, the minor axis may be controlled in the growth of a crystal as well as the major axis. Therefore a 90° crystal was grown so that a minor axis made an angle of about 5° with the normal to the face. This placed the $(20\bar{2}0)$ spot always a few degrees from $\theta=\phi/2$ and provided a wide region for diffuse scattering with its center at $\theta=\phi/2$. To see the advantage of this, compare our Fig. 1 with Fig. 3 in the second paper[2] of this series.

The quantity $D(\phi,\,\theta)$ of (1) was experimentally measured by observing the rate of deflection of the electrometer in the scattering position, Fig. 2, and subtracting the effect due to background as measured with the crystal in the background position, Fig. 2. In this position the drift of the electrometer registers the effect of cosmic rays, α-particles, etc., and the scattering from the air through which the primary beam passes. When the crystal is turned to the background position so that no scattering from the zinc gets into the chamber window, it cuts off the x-rays which are normally scattered from the column of air, indicated by the shaded area of Fig. 2. We therefore corrected for the scattering from the air in the space represented by the shaded area of Fig. 2.

At small angles it becomes necessary to correct for the height of the ionization chamber window and for the height of the primary beam. The effect of both heights is to make the average scattering angle greater than the angle as read on the spectrometer. Calculation showed that when the spectrometer was set at 10° the average scattering angle was about 11°. At settings of greater than 10° the discrepancy between the setting and the average scattering angle became

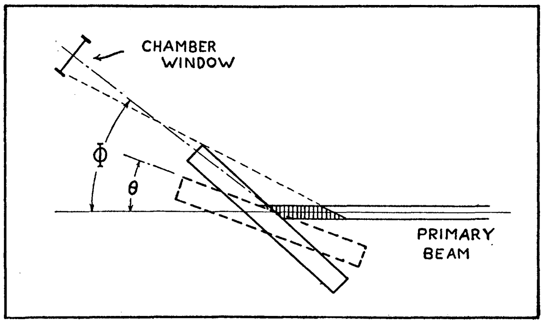

FIG. 2. Showing the necessity of correcting for the scattering from air. Full line rectangle-background position; broken line rectangle-scattering position.

TABLE I. *Values of* $(S\rho/\mu)_{\mathrm{exp}}$ *at 298°K.*

ϕ	$\psi=90°$	14°
10	0.170	
15	.145	0.308
20	.169	.355
25	.183	.343
30	.183	.325
35	.171	.290
40	.160	.238

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[3] G. E. M. Jauncey and W. A. Bruce, paper IV.

less than 1° and the scattering angle was taken as read on the spectrometer.

General radiation with a spectral distribution as shown in Fig. 1 of a previous paper[1] was used.

3. Experimental Results

The results are given in Table I and in Fig. 3. Owing to experimental difficulties, we were unable to obtain a value of $(S\rho/\mu)_{\text{exp}}$ at $\phi=10°$ with the $\psi=14°$ crystal. We obtained the value shown for $\phi=10°$ with the $\psi=90°$ crystal but we feel that due to experimental error the value is too large. However, the value shown was checked by a careful repetition of the experiment at this angle.

According to Zener[4] the diffuse scattering from the valence electrons at small angles falls off as the first power of the scattering angle rather than the second power as does the scattering from the core electrons. This theoretical prediction has been obtained independently by Debye.[5] Recently Scharwächter[6] has obtained results which confirm this theoretical prediction. For a light metal at small angles this effect is measurable, but for zinc it is within the limit of our experimental error and has a negligible effect upon our experimental results.

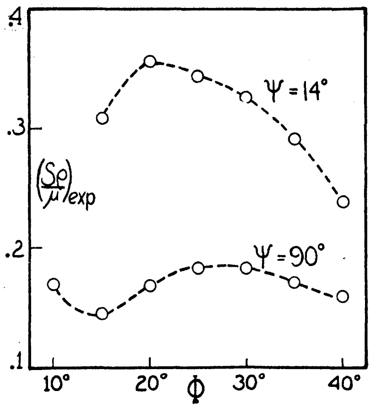

FIG. 3 Experimental values of $(S\rho/\mu)$ plotted against ϕ for $\psi=14°$ and $\psi=90°$.

Discussion of the results of this paper is deferred to the sixth paper of this series.

The authors wish to thank Professor G. E. M. Jauncey for his suggestion of this problem and his aid in refinement of the experimental method.

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[4] C. Zener, Phys. Rev. **48**, 573 (1935).
[5] P. Debye, Physik. Zeits. **38**, 161 (1937).
[6] W. Scharwächter, Physik. Zeits. **38**, 165 (1937).

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Atomic Structure and Vibrations in Zinc Crystals

VI. Determination of Electron Asymmetry and the Two Principal Characteristic Temperatures

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The results reported in papers by Brindley, Miller and the two previous papers of this issue of the *Physical Review* are discussed. The results show that the true atomic structure factor f (the effect of atomic vibrations having been removed) is a function of the orientation angle ψ out to $(\sin\frac{1}{2}\phi)/\lambda=0.6$. It is shown how the f values may be obtained for two values of ψ from diffuse scattering measurements alone at room temperature. The f curves for $\psi=14°$ and 90° coincide for $(\sin\frac{1}{2}\phi)/\lambda$ between 0.6 and 1.0. At 0.6 the curves fork. Correcting Miller's F values ($\lambda=0.71$A) for atomic vibrations and Brindley's F values ($\lambda=1.54$A) for atomic vibrations and dispersion, f points are obtained which mostly fall between or on the f curves for $\psi=14°$ (this is practically the same as the f curve for $\psi=0°$) and $\psi=90°$. It is shown that the difference between the two f curves is due to a reasonable asymmetry in the spatial distribution function of the valence electrons. The ΔF's between Miller's and Brindley's F values are corrected for atomic vibrations, and the resultant Δf's are all equal within experimental error. The average $\Delta f=2.35$ in good agreement with the quantum mechanical $\Delta f=2.36$. The characteristic temperatures associated with vibrations parallel and perpendicular to the principal axis have been found. The characteristic temperature for parallel vibrations decreases while that for perpendicular vibrations remains almost constant with rise of temperature in agreement with Zener's theory. The average characteristic temperature for vibrations in all directions is just slightly greater than the characteristic temperature for specific heat in agreement with Zener's theory. The decrease of the characteristic temperature with temperature appears to begin when the root mean square displacement exceeds about 0.13A.

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