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Anisotropy in the Atomic Vibrations of Zinc Crystals

II. Diffuse Scattering of X-Rays from Single Crystals

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The general radiation from a tungsten tube was used together with Jauncey and Claus' method of integration over all wave-lengths. Because of the high absorption coefficient of zinc it was necessary to scatter the x-rays from the front surface of the zinc crystals. Correction for the presence of fluorescent rays was made. A number of zinc crystals were grown. The control of the direction of the major and minor axes with respect to the surface of the crystal is described. Two types of experiment were made: (1) the variation of S with ψ, the orientation angle, for a fixed value of ϕ, the scattering angle; and (2) the variation of S with ϕ for two fixed values of ψ, one near 90° and the other near 0°. (1) gave remarkable confirmation of the correctness of the form of Zener's formula for the Debye-Waller M for hexagonal crystals, while (2) confirmed in a general way our values as obtained in (1) for a and b in Zener's formula. We find a much higher anisotropy, $a-b=1.66$, than that suggested by Brindley, $a-b=0.785$.

1. INTRODUCTION

As described in the previous article,[1] papers by Zener and by Brindley and Spiers suggested that a study of the diffuse scattering of x-rays from single crystals of zinc should prove of interest. According to the theory of diffuse scattering

$$S=S_{\text{coh}}+S_{\text{inc}}/(1+\alpha \text{ vers } \varphi)^3, \tag{1}$$

where
$$S_{\text{coh}}=(f^2/Z)(1-e^{-2M}) \tag{2}$$

and
$$S_{\text{inc}}=1-(1/Z)\sum E_r^2. \tag{3}$$

Since according to Zener's theory for hexagonal crystals M is related to the angle of orientation ψ by

$$M=(a\cos^2\psi+b\sin^2\psi)\cdot(\sin^2 \tfrac{1}{2}\varphi)/\lambda^2, \tag{4}$$

the diffuse scattering S depends upon the orientation of the crystal. The root-mean-square displacement of an atom in a direction making an angle ψ with the c axis of the crystal is given by[1]

$$(\overline{u_\psi^2})^{\frac{1}{2}}=\{(a\cos^2\psi+b\sin^2\psi)/8\pi^2\}^{\frac{1}{2}}. \tag{5}$$

2. EXPERIMENTAL METHOD

Because of the high absorption coefficient of x-rays in zinc we could not use monochromatic x-rays and used instead the general radiation from a tungsten tube. The spectrum of this radiation is shown in Fig. 1. Also because of the high absorption in zinc we were unable to use the method of transmission through a thin crystal and used instead the method of scattering from the front face as used by the senior author[2] in his original experiments on diffuse scattering.

In Fig. 2, θ is the glancing angle of incidence on the surface of the crystal and ϕ is the angle of scattering. Our angle θ is not to be confused with the θ of the Bragg law. The line BD lies in the plane of scattering and bisects the angle ABC. It is the vibrations of the atom of a crystal in the direction of BD which give rise to the coherent part of the diffuse scattering[3] in the direction BC. The angle ψ is the angle between BD and the c axis of the crystal.

If the Compton effect is neglected the intensity of the scattered rays of wave-length λ is given by[2]

$$I_{\phi,\theta}=(s_\phi A I_0/2R^2\mu_1)\cdot u(\phi,\theta), \tag{6}$$

where I_0 is the intensity of the primary rays of wave-length λ, s_ϕ is the scattering coefficient per unit solid angle in the direction ϕ, μ_1 is the absorption coefficient of the x-rays in the crystal, and

$$u(\phi,\theta)=\frac{2\sin(\phi-\theta)}{\sin(\phi-\theta)+\sin\theta}, \tag{7}$$

In a hexagonal crystal, if the c axis is normal to the plane of scattering in Fig. 2, s_ϕ is not a func-

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[1] G. E. M. Jauncey and W. A. Bruce, Phys. Rev. **50**, 408 (1936). See this article for further references.

[2] G. E. M. Jauncey, Phys. Rev. **20**, 405 (1922). Figs. 2 and 6 in this reference should be interchanged.

[3] G. E. M. Jauncey, Phys. Rev. **37**, 1193 (1931); G. E. M. Jauncey, Phys. Rev. **42**, 453 (1932).

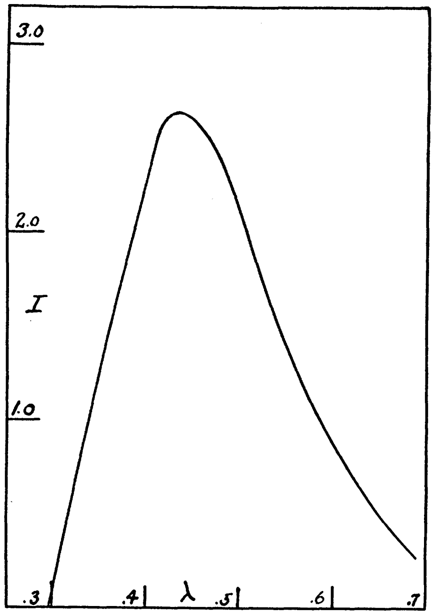

FIG. 1. Spectral distribution curve for the x-rays falling upon the crystal.

tion of θ, so that, if $I_{\phi,\,\theta}/u(\phi,\,\theta)$ is plotted against θ for a given value of ϕ, a horizontal line is obtained except for those values of θ at which Laue spots occur. If the c axis is in some other direction, the graph of $I_{\phi,\,\theta}/u(\phi,\,\theta)$ *vs.* θ will be a monotonic curve except for the Laue spots. We are thus enabled to eliminate the Laue spots as shown in Fig. 3.

From previous papers,[4] we obtain for front face scattering when a band of wave-length is used

$$(S\rho/\mu_1)_{\text{exp}}=\frac{4R^2Wm^2c^4}{ANZe^4(1+\cos^2\phi)}\cdot\frac{D_{\phi,\,\theta}}{D_0u(\phi,\,\theta)},\quad (8)$$

where μ_1/ρ is the mass absorption coefficient of the primary rays of wave-length λ in the crystal, and $D_{\phi,\,\theta}$ and D_0 are, respectively, the ionization currents produced by the scattered and the primary rays. Now, if the distribution-in-wave-length of the intensity in the primary spectrum is $I(\lambda)d\lambda$, we can define another quantity

$$(S\rho/\mu_1)_{\text{th}}=\int(S\rho'/\mu_1)Id\lambda/\int Id\lambda,\quad (9)$$

where, because the Compton effect is taken into account,

$$S'=S_{\text{coh}}+\frac{2K_\phi\mu_1S_{\text{inc}}}{K_0(\mu_1+\mu_2)(1+\alpha\text{ vers }\phi)^3}\quad (10)$$

and μ_2 is the absorption coefficient in the crystal of primary rays of wave-length λ after the Compton change of wave-length. K_ϕ is the fraction of modified rays of original wave-length λ and K_0 the fraction of unmodified rays of this wave-length absorbed in the ionization chamber.

3. METHOD OF GROWING THE CRYSTALS

We used a slight modification of the method described by Cinnamon.[5] Crystals were grown in a Lavite mould of 18 cm length with thermocouples at 6 cm intervals. Instead of a ceramic cover for the mould, a thick strip of mica with a hole for pouring was placed on the mould and was held down by a $\frac{3}{8}$-inch iron bar. The hole was above one end of the mould. A cup of alundum cement was made around the mica hole to facilitate pouring the casting and also to provide an easily accessible cleavage surface. We shall refer to this as the well of the mould. The nucleus used was a wire pulled out by the Czochralski-Gomperz method. The nucleus was placed at the opposite end of the mould from the well. The top surface of the casting in the mould was the surface which was later used for the scattering of x-rays. The available part of this surface measured 12 cm by 1 cm. The thickness of the crystal was 0.6 cm. In most cases the crystals were grown with the c axis perpendicular to the length

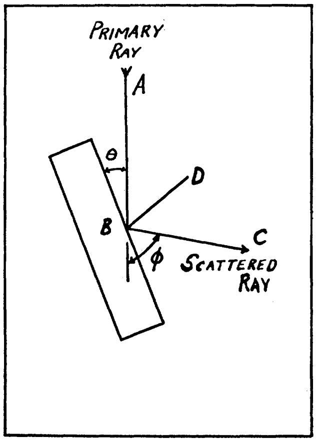

FIG. 2. Scattering from front face.

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[4] G. E. M. Jauncey and W. D. Claus, Phys. Rev. **46**, 941 (1934). See this article for further references.

[5] C. A. Cinnamon, Rev. Sci. Inst. **5**, 187 (1934).

of the crystal but making various angles with the surface of the crystal. By using various crystals a number of values of ψ could thus be obtained in the experiments on the diffuse scattering of x-rays. Also, with one and the same crystal, variation in ψ could be obtained by tilting the crystal about an axis parallel to its length, the length being parallel to the plane of scattering in Fig. 2. In this way it is possible to obtain diffuse scattering measurements for the same value of ψ and ϕ but for crystals with different angles between the c axis and the surface.

The control of the major axis is very simple and in the 90° crystal (i.e., the c axis is perpendicular to the length of the crystal) the minor axis may be placed within one or two degrees. This latter is possible because zinc has a tendency to slip among planes of highest atomic density and to cleave along these planes when cooled to the temperature of liquid air.[6] The portion grown in the well of the mould was useful for finding the direction of the c axis with respect to the surface of the crystal. The growth of the crystal is best under control when the temperature gradient along the casting is about 5°C per cm and the rate of growth about 0.16 cm/min. The crystal casting when finished is covered with oxide. This is removed with 20 percent hydrochloric acid, which leaves a slightly etched surface. Examination of the etching tells whether or not the crystal is single.

If no cleavage can be found along a minor axis the orientation of this axis may be found by carefully examining the bright surface of an exposed basal plane. Faint twinning marks are usually found and indicate the minor axes. These twinning marks do not mean that the crystal is a twin but that when it was cleaved twins started and almost immediately recrystallized leaving only the marks at the very surface of cleavage. A freshly cleaved basal plane surface is highly reflecting and it is a simple matter to determine by optical means the direction cosines of the c axis with respect to the coordinate axes of the spectrometer. The angle θ is also determined by optical means by pasting a mirror on the surface of the crystal. It is interesting to note that diffuse scattering measurements cannot be obtained for $\psi = 0°$ since a Laue spot necessarily occurs at this setting of the crystal. Knowing the directions of the major and minor axes with respect to the spectrometer, the values of θ in Fig. 2 at which Laue spots occur can be predicted and so avoided.

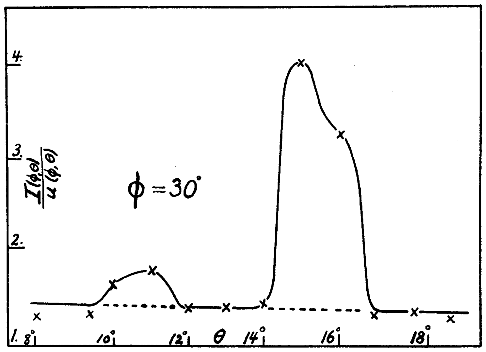

FIG. 3. Method of eliminating Laue spots.

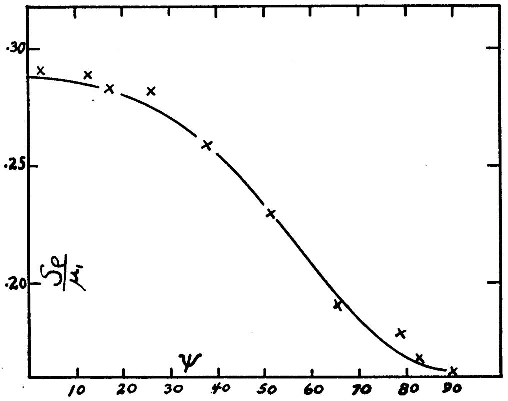

FIG. 4. Variation of diffuse scattering with the angle of orientation for a scattering angle of 30°.

4. CORRECTION FOR FLUORESCENCE RAYS

The x-rays which were used were of shorter wave-length than that of the K absorption edge of zinc and so the K fluorescence radiation of zinc was excited. The fluorescence radiation entering the ionization chamber was considerably reduced by placing 0.0336 cm of aluminum in front of the chamber window. However, a small amount of fluorescence radiation still penetrated into the chamber. By a modification of the method described by Jauncey and DeFoe[7] we were able to correct for this small amount. We found that the part of $(D_{\phi,\,\theta})/D_0$ due to fluorescence radiation

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[6] R. F. Miller, Metals Technology, Tech. Pub. 703 (1936).

[7] G. E. M. Jauncey and O. K. DeFoe, Phil. Mag. **1**, 711 (1926) and Proc. Nat. Acad. Sci. **11**, 520 (1925).

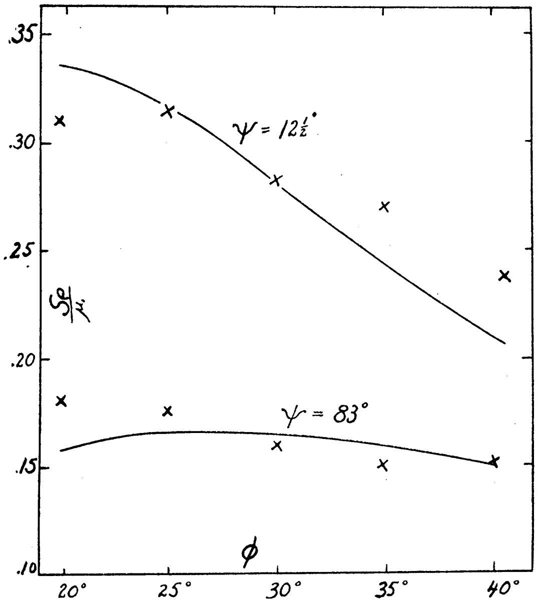

FIG. 5. Variation of diffuse scattering with angle of scattering for fixed values of ψ.

when $\theta=\phi/2$ was $(2.0\pm0.4)\times10^{-7}$. For $\phi=30°$, $\psi=90°$, and $\theta=\phi/2$, the value of $(D_{\phi,\,\theta})/D_0$ due to both fluorescence and scattered rays was 94×10^{-7}. The values for $D_{\phi,\,\theta}/D_0$ corrected for fluorescence radiation are used in (8) for calculating $(S\rho/\mu_1)_{\mathrm{exp}}$. The area A of the ionization chamber window was 0.897 cm^2 and the distance R of the window from the axis of the spectrometer was 12.24 cm.

5. RESULTS FOR THE VARIATION OF ψ FOR A GIVEN VALUE OF ϕ

By using several crystals we were able to obtain values of $(S\rho/\mu_1)_{\mathrm{exp}}$ for various values of ψ between 2.5° to 90° for a fixed scattering angle of 30°. These values of $(S\rho/\mu_1)_{\mathrm{exp}}$ are shown as crosses in Fig. 4. In order to calculate values for plotting $(S\rho/\mu_1)_{\mathrm{th}}$ it was necessary to use quantum-mechanical values of f and ΣE_r^2. We have used Brindley's estimated values[8] of f. Unfortunately Brindley does not give values of ΣE_r^2. We have therefore used ΣE_r^2 values which have been extrapolated from the ΣE_r^2 values for copper given by Compton and Allison.[9] The incoherent part of the diffuse scattering in the case of zinc is only a small fraction of the total diffuse scattering so that the error introduced by using Compton and Allison's ΣE_r^2 values is insignificant. Next, it was necessary to assume values of a and b in (4). We tried various values and found that the values

$$a=2.34\,A^2, \qquad b=0.68\,A^2$$

give the best fit. The curve of $(S\rho/\mu_1)_{\mathrm{th}}$ *vs.* ψ is that shown in Fig. 4. Because of the excellence of the fit between the experimental points and the curve we feel confidence in the above values of a and b. The excellent fit gives remarkable confirmation of the form of Zener's formula (2) for hexagonal crystals containing atoms of one kind. Putting these values of a and b in (5), we obtain the root-mean-square displacements reported in the previous paper.[1]

6. RESULTS FOR THE VARIATION OF ϕ FOR TWO VALUES OF ψ

We used two crystals, one with $\psi=12.5°$ and the other with $\psi=83°$, and obtained values of $(S\rho/\mu_1)_{\mathrm{exp}}$ for scattering angles ranging from 20° to 40°. The experimental values are shown as crosses in Fig. 5. The curves are graphs of $(S\rho/\mu_1)_{\mathrm{th}}$ *vs.* ϕ for $\psi=12.5°$ and $\psi=83°$, respectively. The values of a and b shown in the preceding section have been used in calculating values of $(S\rho/\mu_1)_{\mathrm{th}}$. The points do not fall upon the curves as well as we would like. However, there was some trouble with Laue spots at $\phi=40°$ so that the value of $(S\rho/\mu_1)_{\mathrm{exp}}$ at this angle is somewhat unreliable. Also at $\phi=20°$ the theoretical f and ΣE_r^2 values which are used in calculating $(S\rho/\mu_1)_{\mathrm{th}}$ are somewhat uncertain. At any rate our points do show a big difference between the diffuse scattering for $\psi=12.5°$ and that for $\psi=83°$ over the range of scattering angles investigated. The points roughly follow the trend of the curves. All of the points demand values of a and b that are distinctly greater than Brindley's values of a and b shown in Table I of our first paper[1] and still greater than Zener's values for the modified Debye model. Perhaps it is still more important that our value for the anistropy is $a-b=1.66$ as compared with Brindley's value 0.785 and Zener's value 0.465.

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

[9] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, p. 782.