

Anisotropy in the Atomic Vibrations of Zinc Crystals.

III. The (0002) and (10 $\bar{1}$ 0) Reflections of Mo $K\alpha$ X-Rays from Powdered Zinc

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The ratio of the F value for the (0002) reflection to the F value for the (10 $\bar{1}$ 0) reflection of Mo $K\alpha$ x-rays from powdered zinc was found to be 0.891. This compares very well with Brindley's value of 0.894. Our results suggest that the value of F for the (10 $\bar{1}$ 1) reflection of Cu $K\alpha$ rays is 20.1, which is somewhat higher than Brindley's value.

BRINDLEY¹ first noticed that the F value for the (10 $\bar{1}$ 0) reflection is much greater than that for the (0002) reflection when Cu $K\alpha$ x-rays are used. Hence Brindley has applied the term anomalous to the (10 $\bar{1}$ 0) reflection. He has suggested that this high value may be due to an impurity, but he finds a similar result for the same reflection from cadmium.² However, it is possible that the difference between these two reflections is partially due to anisotropy in the vibrations of the atoms and perhaps partially due to the asymmetry of the electron structure of the atoms in the zinc crystals, as pointed out by Jauncey and Bruce.³ Since Brindley's results were obtained by a photographic method for Cu $K\alpha$ x-rays, it is important to determine whether the same difference between $F(0002)$ and $F(10\bar{1}0)$ is obtained when Mo $K\alpha$ rays are used and when the observations are made by means of an ionization chamber instead of by a photographic film.⁴

The method used was that described by Wollan.⁵ Very fine zinc powder was prepared by the sublimation of pure zinc filings heated in a vacuum to prevent oxidation, as described by Brindley and Spiers.⁶ X-rays from a molybdenum target tube operated at 32 kv peak and 29 ma fell upon the briquet of zinc powder at a glancing angle, α , of 8° 35'. A zirconium filter was placed in front of the ionization chamber and thus absorbed not only the Mo $K\beta$ line but also the fluorescent zinc K radiation. The slit before the ionization chamber was curved to a radius corresponding to

that of the average curvature of the (0002) and (10 $\bar{1}$ 0) lines. Its width was 1 mm at a distance of 14.8 cm from the axis of the spectrometer. Our results are shown in Fig. 1 and are the average of several runs over the range of scattering angles shown. In this figure the hump for the (10 $\bar{1}$ 1) reflection is also shown. The ratio of the area under the (0002) hump to that under the (10 $\bar{1}$ 0) hump is 1.156, while the ratio of the heights of the two maxima is 1.150. Now,

$$\text{Area} = \text{const.} \cdot p s_c^2 \left(\frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \right) \frac{\sin (2\theta - \alpha) F^2}{\sin (2\theta - \alpha) + \sin \alpha}, \quad (1)$$

where p is the number of planes cooperating in producing the reflection, s_c is the crystal structure

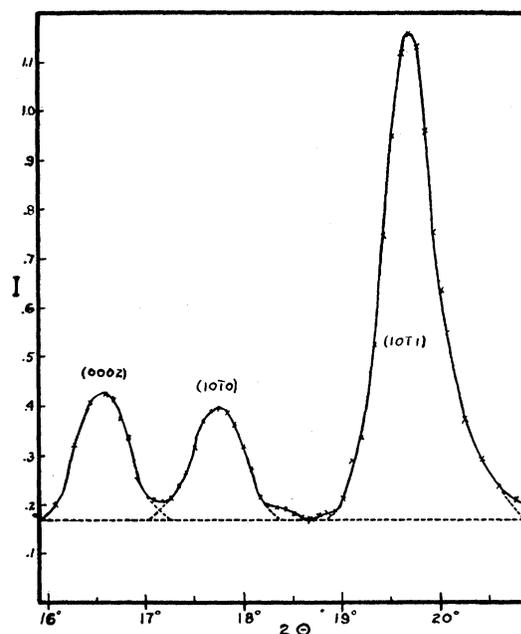


FIG. 1. Intensity of scattering against scattering angle.

¹ G. W. Brindley, *Phil. Mag.* **21**, 790 (1936).

² G. W. Brindley, *Proc. Leeds Phil. Soc.* **3**, 200 (1936).

³ G. E. M. Jauncey and W. A. Bruce, *Phys. Rev.* This issue.

⁴ For notation used in the above paragraph, see reference 3.

⁵ E. O. Wollan, *Phys. Rev.* **35**, 1019 (1930).

⁶ G. W. Brindley and F. W. Spiers, *Phil. Mag.* **20**, 865 (1935).

TABLE I. *F* values.

Reflection	θ	Area	Relative <i>F</i>	
			Mo <i>K</i> α	Cu <i>K</i> α
0002	8° 17'	1.156	0.891	0.897
10 $\bar{1}0$	8° 54'	1.000	1.000	1.000
10 $\bar{1}1$	9° 49'	4.72	.898	.866

The (10 $\bar{1}1$) reflection of the β -line falls very nearly on the (10 $\bar{1}0$) reflection of the α -line. The areas in the figure are uncorrected. Measurement of the spectrum of the rays penetrating the zirconium filter give $\beta/\alpha=0.5/100$. The *F* values are for pure *K* α rays.

factor (2 for (0002), 1 for (10 $\bar{1}0$), $\sqrt{3}$ for (10 $\bar{1}1$)), θ is the Bragg angle of reflection, and *F* is the atomic structure factor including the effect of thermal vibrations. From the ratio of the areas the ratio of the *F*'s may be obtained. Our final results are shown in Table I. The ratios $F(0002)/F(10\bar{1}0)$ and $F(10\bar{1}1)/F(10\bar{1}0)$ as found by us are shown in the fourth column while Brindley's ratios are shown in the fifth column of the table.

Because of dispersion,¹ the *f* values (i.e., *F* values corrected for thermal vibration) should be greater by 2.14 when Mo *K* α rays are used than when Cu *K* α rays are used. Hence our value of

$F(0002)/F(10\bar{1}0)$ should be slightly less than Brindley's value. Our estimate of Brindley's value for Mo *K* α rays is 0.894, which is in very good agreement with our value of 0.891. Our estimate of Brindley's value of $F(10\bar{1}1)/F(10\bar{1}0)$ for Mo *K* α rays is 0.863. We feel that this is really lower than our value of 0.898.

Since Brindley made repeated experiments on $F(10\bar{1}0)$, we take his value of 22.4 for Cu *K* α rays to be correct. From our ratio, given above, is obtained $F(10\bar{1}1)=20.1$. If this value is used in Fig. 1 of Jauncey and Bruce's paper,³ and $f(10\bar{1}1)$ found by using their values of *a* and *b*, the *f* point falls between the curve for $\psi=0^\circ$ which passes through the *f* point for (0002) and the curve for $\psi=90^\circ$ which passes through the *f* point for (10 $\bar{1}0$). This fact gives some support to the idea of asymmetry in the electron structure of the atoms.³

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Fundamental Absorption Bands of the Deuteroammonias

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The four fundamental vibration bands of ND₃ have been observed in infrared absorption, ν_3 being a double band as in NH₃. The frequencies of the parallel vibrations, expressed in cm⁻¹, are $\nu_1=2420$, $\nu_3=749.2$ and 745.8, and of the perpendicular vibrations, $\nu_2=2556$ and $\nu_4=1191.3$. The rotational structure for ν_3 is completely resolved. The perpendicular bands consist of many components with zero branches spaced at intervals of 1.7 cm⁻¹ in ν_2 and 5.2 cm⁻¹ in ν_4 . The former cannot be resolved: they coalesce into a broad central absorption region, but the spacing of the most intense rotation lines in the composite band indicates the interval between centers. These frequency intervals agree well with the predictions of Johnston and Dennison. The moments of inertia for ND₃ are determined from the

structure of the band ν_3 , by comparison with observations upon NH₃. They are $C=8.985 \times 10^{-40}$ g cm² with respect to the symmetry axis, and $A=5.397 \times 10^{-40}$ g cm² for any perpendicular axis. From these the molecular dimensions are obtained. The height of the pyramid is 0.360×10^{-8} cm and the distance between hydrogen atoms is 1.645×10^{-8} cm. New information regarding the potential curve is obtained (1) from observations upon the doubling of the first excited levels in the four varieties of ammonia, and (2) from the positions of higher excited levels in ND₃. Four vibration levels are located which lie above the central potential hump, and correspond to oscillations of the nitrogen atom from side to side through the plane formed by the hydrogen atoms.

THE ammonia molecule is known to have the form of a low equilateral triangular pyramid. Its spectrum is rich, including many harmonic and combination bands in addition to

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the four fundamental frequencies, but the analysis and interpretation of the available observations is by no means complete. The moment of inertia *A* with respect to an axis normal to the symmetry line may be obtained immediately