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The Anomalous Dispersion of X-rays by Single Crystal ZnSe

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An X-ray photographic method is described which allows the (111) and ($\bar{1}\bar{1}\bar{1}$) faces of a suitably prepared slice of a single crystal of ZnSe to be distinguished. Etching in hot concentrated HCl produces triangular pits on the (111), zinc face, but merely roughens the ($\bar{1}\bar{1}\bar{1}$) selenium face.

1. Introduction

The direction of the polar axis in compound semiconductors with the zinc blende and wurtzite structures is important in connection with etching and dislocation studies and with the growth of epitaxial layers and bulk crystals. For many of the III-V and II-VI compounds the absolute configuration of the polar axis has previously been determined by measuring the difference in the intensities of X-rays scattered from opposite faces, which are normal to the polar axis. This has either been done at fixed wavelengths [1-8], for example by using characteristic emission lines, or over a short range of wavelengths which spans the K-absorption edge of one of the constituent atoms [8-10]. Since accurate intensity measurements are required most workers have used diffractometric techniques rather than less exact photographic methods. However, little attention has been paid to the differences in the shapes of the X-ray intensity spectra reflected from opposite (111) or (0001) faces, although such differences can be revealed by simple photographic techniques.

In this note a photographic technique is described which allows the intensities of X-rays diffracted from opposite polar faces of cubic ZnSe to be measured as a function of wavelength. The measured intensity distributions are compared with the calculated X-ray spectra and good agreement is obtained.

2. Experimental

A (111) slice of ZnSe was cut from a bulk sample, grown from the vapour phase by the method described by Burr and Woods [11]. The slice was ground and mechanically polished down to 0.25 μm diamond size, and then chemically polished in a mixture of orthophosphoric acid and chromic oxide to which hydrochloric acid had been added, to remove the surface damage. After that the sample was mounted on a Unicam S25 goniometer and orientated so that the Bragg reflections spanned the required wavelength range as the sample was rocked about its vertical axis. The unfiltered radiation from a Philips fine focus X-ray tube with a copper target provided a suitably intense continuous spectrum. The radiation was collimated to obtain a beam, 0.25×3 mm in section, with an angular divergence of less than 4′ of arc. The X-ray film was placed some 90 mm from the sample, and the beam width at the film was 0.04 mm. After 70 h exposure the optical density of the film was recorded using a microdensitometer and the diffracted X-ray intensity was plotted as a function of position on the plate.

For best results it is desirable to use as high an X-ray intensity as possible while scanning the appropriate range of wavelength. However, since the X-ray intensity is proportional to the square of the applied voltage, too high an intensity will lead to the production of short wavelength X-rays and high order reflections will be superimposed on the required (111) reflections. For this reason the tube voltage was limited to 17.6 kV and a wavelength band extending from 0.7 to 1.7 Å was used. This range embraces the K-absorption edges of Zn at 1.28 Å and Se at 0.98 Å. The angle through which the crystal was rocked was about 10°.

3. Calculation of Reflected Intensities

According to James [12] the total X-ray energy E, reflected by a crystal being rocked at an angular velocity ω is

$$E = \frac{I_0}{\omega}\left(\frac{1 + \cos^2 2\theta}{\sin 2\theta}\right)\frac{K\lambda^3}{\mu}\,|F|^2$$

I_0 is the incident X-ray intensity. The bracketed term is the Lorentz Polarisation Factor (LPF) which is a function of the angle of incidence θ between the beam and the diffracting plane. λ is the wavelength for Bragg reflection, μ is the linear absorption coefficient at that wavelength. F is the appropriate structure factor and K is a constant which need not be known.

The LPF can be obtained from tables [13] and μ for ZnSe at a wavelength λ can be calculated from

$$\left.\frac{\mu}{\rho}\right)_{\text{ZnSe}} = \frac{\text{Zn}}{\text{ZnSe}}\left.\frac{\mu}{\rho}\right)_{\text{Zn}} + \frac{\text{Se}}{\text{ZnSe}}\left.\frac{\mu}{\rho}\right)_{\text{Se}}$$

ρ is the density, hence μ/ρ is the mass absorption coefficient. Zn/ZnSe and Se/ZnSe are the mass ratios of Zn and Se in ZnSe. The values of $\mu/\rho)_{\text{Zn}}$ and $\mu/\rho)_{\text{Se}}$ were also obtained from tables [14, 15] although a certain amount of interpolation was necessary.

The wavelength was related to the position on the photographic plate from geometrical considerations. The superimposed characteristic copper K_α and K_β lines from the target served as an additional calibration. Tungsten L emission was also observed (even though a copper target was used) and these lines were also used for calibration purposes. The wavelength scale proved to be almost linear.

If the unit cell is chosen with a Zn atom at the origin [8]

$$F_{(111)} = 4f_{\text{Zn}} - 4if_{\text{Se}}$$

and $$F_{(\bar{1}\bar{1}\bar{1})} = 4f_{\text{Zn}} + 4if_{\text{Se}}$$

f_{Zn} and f_{Se} are the atomic scattering factors. In general these are complex, and can be written $f = f_0 + \Delta f' + i\Delta f''$ [12], where f_0 is the scattering factor derived on the assumption of negligible resonance absorption of the incident X-ray beam in the sample. $\Delta f'$ and $\Delta f''$ are the real and imaginary parts of the correction required when absorption is taken into account. These terms are of most significance in the vicinities of the main X-ray absorption edges. The values of f_0 used for the $\{111\}$ reflection of ZnSe were those appropriate to Zn° and Se°, namely 25.70 and 28.46 [17]. We have preferred to regard the crystal as composed of atoms rather than ions, in view of the considerable covalent bonding of ZnSe [18]. Values of $\Delta f'$ and $\Delta f''$ were obtained from James [12] and plotted as a function of wavelength. These values represent the effects of K absorption only. L and M absorption has been considered by Dauben and Templeton [16], but only at three wavelengths. Using the curves obtained from James' data to give the shape of the correction function, Dauben and Templeton's values were plotted and interpolated at intermediate wavelengths.

The intensity I_0 of the incident X-ray beam varies considerably with wavelength. We have used the expression given by Stephenson [19] to describe the intensity distribution of the X-ray continuum, i.e.

$$I_0 = \frac{1}{\lambda^2}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)$$

Here λ_0 is the minimum wavelength emitted, which depends on the tube voltage. In our investigations λ_0 was nominally 0.7 Å.

The angular velocity ω was assumed to be constant. To test the validity of this assumption and to check the expression for the X-ray continuum, a separate experiment was performed to determine the shape of I_0/ω as a function of wavelength. This was done by using a crystal of NaCl cut in the $\{111\}$ orientation. The d_{111} spacing for NaCl has a value of 3.255 Å which matches that of ZnSe (3.272 Å) very closely. The L absorption effects are minimal in NaCl over the wavelength range of interest so that the tabulated values for K-shell scattering factor corrections given by James are sufficient.

The results of this experiment indicated that the expression for the distribution of intensity in the continuum was accurate to within 10%, but that ω, although constant over the central range of the traverse, was lower at both ends. This was probably the effect of wear in the work drive cam. In consequence the wavelength range of interest was scanned using the mid-position of the cam drive.

When all the considerations described in this section were taken into account the intensities of X-rays expected to be reflected from the (111) and $(\bar{1}\bar{1}\bar{1})$ faces of ZnSe could be calculated. The results are shown in fig. 1. The curves show that the (111) reflection should be the weaker between the two K absorption edges. The (111) surface corresponds to the zinc face and the $(\bar{1}\bar{1}\bar{1})$ to selenium.

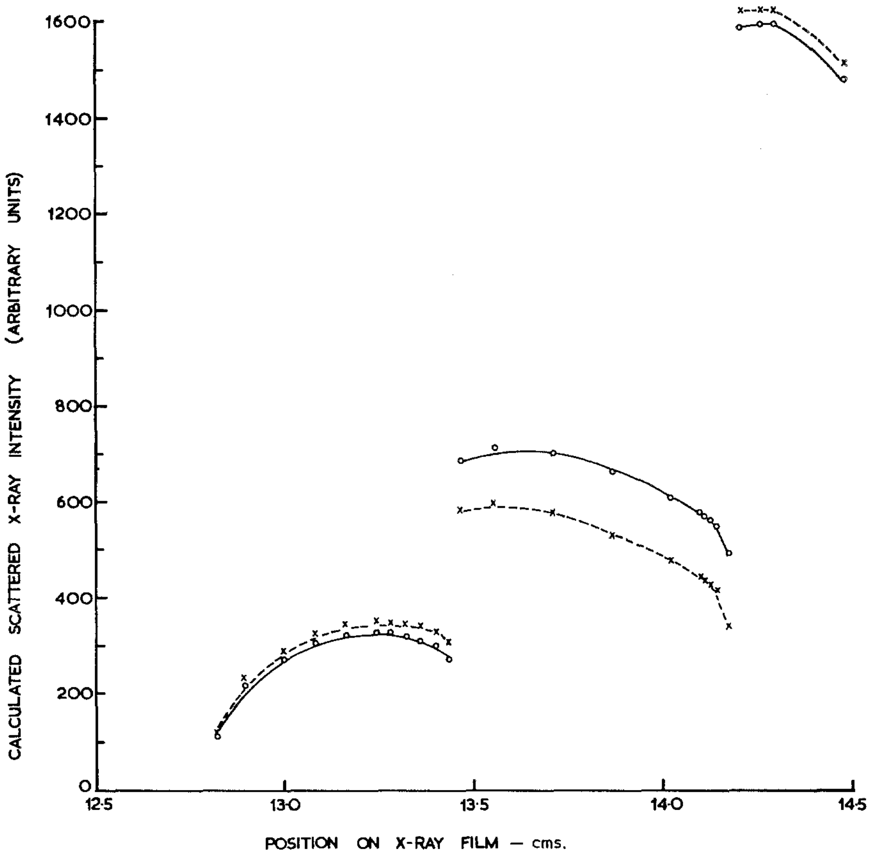

Figure 1 The calculated scattered X-ray intensity from $(\bar{1}\bar{1}\bar{1})$ ——o——, and (111) x-x-x-x, faces of ZnSe.

4. Experimental Results

X-ray reflection spectra from the two faces of a {111} slice of ZnSe were recorded on a photographic plate (Ilford Industrial G) during a 70 h exposure. The optical densities of the two spectra as determined with the microdensitometer are shown in fig. 2. The optical density is proportional to the X-ray intensity. The background intensity at points on the photographic plate, which lay just beyond the limits of the Bragg reflection spectrum, was taken as a measure of the incoherent scattering, and this was subtracted from the measured intensities to obtain the results shown in fig. 2. The overall accuracy of the X-ray intensity measurement was estimated to be about ± 5%; the limit being set by the grain size of the X-ray film used. However, the curves in fig. 2 clearly exhibit the features of anomalous scattering predicted by the calculated curves of fig. 1. Thus the intensity level in the middle wavelength range between the two K-absorption edges is much lower for one of the reflections than for the other. In addition the expected inversion of the relative scattered intensities occurs about each absorption edge. On this basis it is concluded that the curve denoted by the crosses in fig. 2 is associated with scattering from a (111), zinc face, whereas that denoted by circles corresponds to scattering from a $(\bar{1}\bar{1}\bar{1})$, selenium face.

It is well known that chemical etching produces different effects on the opposite polar faces of crystals with the zinc blende structure. However, etching alone does not allow one to determine which face is a (111) plane and which a $(\bar{1}\bar{1}\bar{1})$. When ZnSe is etched in hot concentrated HCl, triangular etch pits are formed on one face, whereas an overall matte finish is produced on the other [11, 20]. By etching the crystal used in the X-ray examination described here we have been able to demonstate that the triangular pits are formed on the (111), zinc face. The $(\bar{1}\bar{1}\bar{1})$, Se face is merely roughened.

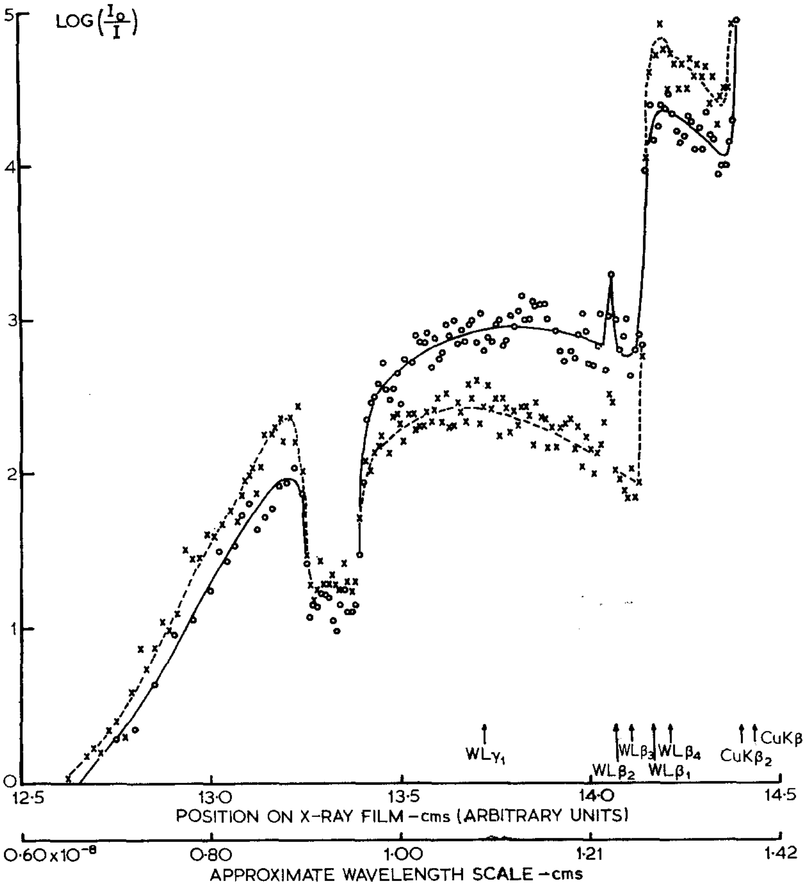

Figure 2 Experimental X-ray scattering curves for ZnSe. Comparison with fig. 1 shows that o-o-o-o is for scattering from a ($\bar{1}\bar{1}\bar{1}$) face, whereas x-x-x-x corresponds to scattering from a (111) face.

5. Discussion

The results described here show that the determination of the polarity of a (111) slice of a crystal of ZnSe is well within the capabilities of a simple photographic method, and there is good agreement with the earlier work of Mariano and Wolff [8] who investigated anomalous scattering from a number of III-V and II-VI compounds including ZnSe. What interpretation can be placed on the finer differences between the measured and calculated curves depends clearly on the accuracy of the photographic and operational procedure. The measured step heights on crossing the K-absorption edges are less than the mosaic theory would predict, but Cole and Stemple [10] have shown that such a result would be expected for a crystal with perfection better than mosaic.

The extension of this simple photographic technique to other non-centrosymmetric structures and to pseudo-binary semiconductors in particular, is limited by the requirements of the Bragg condition itself and by the lack of information about the positions of the constituent atoms in the unit cell. For example, if the "d" spacing of the relevant reflecting plane is larger, and the wavelength range spanning the K-absorption is 0.2 to 1.0 Å then the angle of incidence is necessarily of the order of 1°, and a much finer beam or larger crystal would be essential. An alternative approach would be to use the range 0.7 to 2.0 Å and utilise the anomalous dispersion between the K and L absorption edges. Although this had been neglected in the early work there is theoretical [16] and experimental [21] evidence which indicates that differences in the reflected intensities are considerable at wavelengths well removed from the absorption edges. It has only to be noted that the X-ray absorption coefficient increases steeply as the wavelength is increased from the K to L absorption regions, to appreciate that the preceding statement is correct.

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References

1. D. COSTER, K. S. KNOL, and J. A. PRINS, *Z. Physik.* **63** (1930) 345.
2. J. G. WHITE and R. C. ROTH, *J. Appl. Phys.* **30** (1959) 946.
3. E. P. WAREKOIS, M. C. LAVINE, A. N. MARIANO, and H. C. GATOS, *ibid* **33** (1962) 690; **37** (1966) 2203.
4. E. P. WAREKOIS and P. H. METZGER, *ibid* **30** (1959) 960.
5. R. ZARE, W. R. COOK, JNR., and L. R. SHIOZAWA, *Nature* **189** (1961) 217.
6. K. BRACK, *J. Appl. Phys.* **36** (1965) 3560.
7. O. BRAFMAN, E. ALEXANDER, B. S. FRENKEL, Z. H. KALMAN, and J. T. STEINBERGER, *ibid* **35** (1964) 1855.
8. A. N. MARIANO and G. A. WOLFF, *Z. Krist*, **126** (1968) 244.
9. A. N. MARIANO and R. E. HANNEMAN, *J. Appl. Phys.* **34** (1963) 384.
10. H. COLE and N. R. STEMPLE, *ibid* **33** (1962) 2227.
11. K. F. BURR and J. WOODS, *J. Cryst. Growth*, in press.
12. R. W. JAMES, "Optical Principles of the Diffraction of X-rays" (G. Bell and Sons Ltd., London, 1958).
13. J. S. KASPER and K. LONSDALE (eds.) International Tables for X-ray Crystallography (International Union of Crystallography, Birmingham 1959). Vol. II
14. R. C. WEAST (Ed.) Handbook of Chemistry and Physics (The Chemical Rubber Co., Cleveland, Ohio).
15. Handbuch der Anorganischen Chemie (Gmelin-Verlag G.M.B.H. 1949), Vol. 10 Al. p. 231.
16. C. H. DAUBEN and D. H. TEMPLETON, *Acta Cryst.* **8** (1955) 841.
17. J. S. KASPER and K. LONSDALE (Eds.) International Tables for X-ray Crystallography (International Union of Crystallography, Birmingham 1959). Vol. III.
18. W. L. ROTH, Physics and Chemistry of II-VI Compounds, Eds. M. Aven and J. S. Prener. (North-Holland Publishing Co. Amsterdam 1967), Chap. 3.
19. S. T. STEPHENSON, Encyclopedia of Physics, Ed. S. Flugge (Springer-Verlag, Berlin, 1957), Vol. 30, p. 337.
20. A. SAGAR, W. LEHMANN, and J. W. FAUST JR., *J. Appl. Phys.* **39** (1968) 5336.
21. S. W. PETERSON, *Nature* **176** (1955) 395.

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