

tum, in order to reduce absorption of the radiation by the europous salts.

Diffraction patterns of EuSO_4 and EuCO_3 were indexed, and in both cases the unit cells were found to be orthorhombic. The lattice constants and densities are given in Table 1 and compared with the respective constants for the strontium salts. Pauling's values for EuSO_4 are also given in brackets. Calculated and observed $1/d^2$ values are given in Table 2; good agreement between these values has been obtained.

Further examination of the patterns shows that EuSO_4 is isomorphous with SrSO_4 and has the BaSO_4 structure type with space group $Pnma$ (D_{2h}^{16}) and four molecules in the unit cell, while EuCO_3 has a KNO_3 type structure, the space group being $Pm\bar{c}n$ ($Pnma$) (D_{2h}^{16}), and four molecules in the unit cell.

Discussion

Comparison of the lattice constants of EuSO_4 found in this work with those obtained by Pauling shows that dimensions of the unit cell of EuSO_4 are somewhat smaller than reported by him. Pauling himself pointed out that there is some uncertainty in his results. On the other hand, as there is good agreement between the standard pattern and our measurements on SrSO_4 , it may be assumed that there was no absorption error in our case to cause deviation of our results from those of Pauling. Moreover, the good agreement between the observed and calculated values of $1/d^2$, as well as of the density, leaves little doubt as to the reliability of the present results.

Crystal data of divalent europium compounds have been used by many authors to calculate the ionic radii of Eu^{2+} . Pauling, who found the lattice constants

of EuSO_4 to be higher than those of SrSO_4 , assumes the ionic radius of Eu^{2+} to be 1.17 Å ($\text{Sr}^{2+}=1.13$ Å). Ketelaar also lists a somewhat higher value for the ionic radius of Eu^{2+} (1.14 Å) than for Sr^{2+} (1.10 Å) (Ketelaar, 1958). On the other hand, the lattice constants of the sulphide, selenide and telluride (Klemm & Senff, 1939) and the oxide (Eick, Baenziger & Eyring, 1956) of divalent europium, all with an NaCl type structure, were found to be slightly smaller than the lattice constants of the corresponding isomorphous strontium compounds. Hence the ionic radius of Eu^{2+} given by the above investigators is smaller by 0.03 Å than that of Sr^{2+} .

The lattice constants of EuSO_4 and EuCO_3 in the present work indicate that the ionic radii of Eu^{2+} and Sr^{2+} are equivalent, that of europium being somewhat smaller, certainly not larger, than that of strontium.

References

- COOLY, R. A. & YOST, A. M. (1946). *Inorganic Syntheses*. Vol. II, p. 70. New York: McGraw-Hill.
- EICK, H. A., BAENZIGER, N. C. & EYRING, L. (1956). *J. Amer. Chem. Soc.* **78**, 5147.
- GLASNER, A., LEVY, E. & STEINBERG, M. (1963). *J. Inorg. Nucl. Chem.* **25**, 1415.
- KETELAAR, I. A. A. (1958). *Chemical Constitution*. p. 29. Amsterdam: Elsevier.
- KLEMM, W. & SENFF, H. (1939). *Z. anorg. Chem.* **241**, 259.
- PAULING, L. (1937). *J. Amer. Chem. Soc.* **59**, 1132.
- SWANSON, H. E. & FUYAT, R. K. (1953). *Nat. Bur. Stand. Circular* 539, Vol. II, 61.
- SWANSON, H. E., FUYAT, R. K. & UGRINIC, G. M. (1954). *Nat. Bur. Stand. Circular* 539, Vol. III, 56.

Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.

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A note on the determination of phases by anomalous dispersion. By G. A. SIM, *Chemistry Department, The University, Glasgow, W. 2, Scotland*

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The differences which arise between the intensities $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$, when anomalously scattering atoms are present in a non-centrosymmetric unit cell, offer access to the phases of the reflexions. Two solutions, α_1 and α_2 , are normally obtained for each independent reflexion and it appears to be customary to decide between these alternatives by adopting the value closer to the heavy-atom phase, α_H (see, e.g., Dale, 1962; Hall & Maslen, 1964). While this undoubtedly selects the more probable phase for each reflexion it does not necessarily lead to

the best electron-density distribution. To minimize the mean-square error in electron density each phase solution should be included with a weight proportional to the probability of its being the correct choice (cf. Woolfson, 1956; Dickerson, Kendrew & Strandberg, 1961).

It has been shown (Sim, 1959) that the probability of obtaining a value of $(\alpha - \alpha_H)$ between ξ and $\xi + d\xi$ is given by

$$p(\xi)d\xi = \exp(X \cos \xi) d\xi / 2\pi I_0(X),$$

where

$$X = 2|F| |F_H| / \Sigma f_L^2.$$

It follows that

$$\frac{\text{Probability of } \alpha_1 \text{ being correct choice}}{\text{Probability of } \alpha_2 \text{ being correct choice}} = \frac{\exp [X \cos (\alpha_1 - \alpha_H)]}{\exp [X \cos (\alpha_2 - \alpha_H)]}$$

and the terms in the Fourier series representing the 'best' electron-density distribution are of the form

$$w|F| \exp (i\alpha_1) + (1-w)|F| \exp (i\alpha_2),$$

where

$$w = \frac{\exp [X \cos (\alpha_1 - \alpha_H)]}{\exp [X \cos (\alpha_1 - \alpha_H)] + \exp [X \cos (\alpha_2 - \alpha_H)]}$$

When the crystal contains only one type of anomalous scatterer the phase solutions α_1 and α_2 are most conveniently expressed (Ramachandran & Raman, 1956) as

$$\begin{aligned} \alpha_1 &= \alpha_H + \pi/2 - \theta \\ \alpha_2 &= \alpha_H + \pi/2 + \theta \end{aligned}$$

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Double Bragg scattering of X-rays in irradiated beryllium oxide. By R. M. MAYER* and T. M. SABINE, *Australian Atomic Energy Commission Research Establishment, Lucas Heights, N.S.W., Australia*

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Double Bragg scattering of X-rays occurs when two or more reciprocal lattice points intersect the Ewald sphere so that the once-reflected beam is diffracted by a second set of planes. This produces a reflexion which is forbidden by normal space group considerations. This phenomenon, previously observed in substances like diamond (Renninger, 1937) and germanium (Cole, Chambers & Dunn, 1962), has now been detected in beryllium oxide during a study of the effects of neutron irradiation.

As BeO has the wurtzite structure the forbidden reflexions within the $\text{Cu } K\alpha$ sphere are those $h\bar{h}2hl$ reflexions for which $l = 2n + 1$. The crystal examined was a thin flake of basal plane habit, which had been irradiated to a dose of 2.5×10^{20} nvt at $75 - 100^\circ\text{C}$ (> 1 MeV). A Buerger precession photograph of the $h0l$ reciprocal lattice plane showing the forbidden 001 reflexions as well as pronounced streaking along the reciprocal lattice rods $10l$, $20l$. The streaking can be satisfactorily explained in terms of extrinsic stacking faults in the (001) planes of the hexagonal lattice (Sabine, 1964). However, it seemed unreasonable that sharp superlattice reflexions could be produced by irradiation.

A more detailed investigation was subsequently made with a General Electric Goniostat and a proportional counter. Reflexions 001, 003, 005, as well as 111 and 113 were detected. The intensity distribution of the forbidden 001 reflexions was examined by rotating the crystal about the respective scattering vectors of the reflecting planes. A series of peaks was observed, which repeated every 60° of azimuth and was symmetrical about the midpoint of each range. The reflexions were identified

where θ can be calculated in a direct manner from the Bijvoet inequality $\Delta|F|^2$. It can then be shown that

$$w = [1 + \exp(-2X \sin \theta)]^{-1}.$$

References

- DALE, D. (1962). Thesis, Oxford Univ.
 DICKERSON, R. E., KENDREW, J. C. & STRANDBERG, B. E. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, ed. PEPINSKY, R., ROBERTSON, J. M. & SPEAKMAN, J. C., p. 236. Oxford: Pergamon Press.
 HALL, S. R. & MASLEN, E. N. (1964). *Acta Cryst.* **17**, In the press.
 RAMACHANDRAN, G. N. & RAMAN, S. (1956). *Curr. Sci.*, **25**, 348.
 SIM, G. A. (1959). *Acta Cryst.* **12**, 813.
 WOOLFSON, M. M. (1956). *Acta Cryst.* **9**, 804.

by calculation of the crystal settings which gave rise to simultaneous intersection of the Ewald sphere by two reciprocal lattice points. When one of these reflexions was itself forbidden, no peak was observed. The results of this examination are shown in the Table 1.

The azimuthal position of the multiple scattering peaks is rather sensitive to a change in lattice parameters. Significant shifts from some of the unirradiated peak positions were observed and calculation showed that within the limits of experimental error these fitted the lattice parameters reported by Walker, Mayer & Hickman (1964).

The crystal was then annealed for one hour at 1400°C , at which temperature other techniques indicate that irradiation damage effects disappear (Hickman & Pryor, 1964). Reflexions resulting from planes with high indices could now be detected. This is in accordance with other X-ray diffraction studies (Walker, Mayer & Hickman, 1964) in which it has been found that the higher the ratio $l^2:h^2+hk+k^2$ for a given reflexion, the greater is the radiation-induced broadening. Identical measurements were carried out on an unirradiated crystal of similar habit. Double Bragg scattering was also observed in this crystal and was comparable in intensity with that of the irradiated crystal annealed at 1400°C .

To ensure that recovery of irradiation damage was complete, the crystals were annealed at 1600°C . In both cases, the intensity of the forbidden reflexions increased, the increase being more noticeable for the irradiated crystal. The reason for this increase is not known. It seems more probably due to recovery of imperfections introduced during growth than to further recovery of irradiation damage.

It has been shown by other techniques (Sabine, Pryor

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