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Influence of mosaicity on the Bragg reflexion of polarized X-rays. By S. RAMASESHAN and G. N. RAMACHANDRAN,* *Department of Physics, Indian Institute of Science, Bangalore 3, India*

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When the incident X-rays are unpolarized, the integrated reflexions for a mosaic and a non-absorbing perfect crystal (ϱ_M and ϱ_P respectively) are given by

$$\varrho_M = \frac{1}{2\mu} \frac{l^2}{m^2 c^4} N^2 |F_H|^2 \frac{\lambda^3}{\sin 2\theta} \frac{(1 + \cos^2 2\theta)}{2} = R_M (1 + \cos^2 2\theta), \quad (1a)$$

$$\varrho_P = \frac{8}{3\pi} \frac{l}{m c^2} N |F_H|^2 \frac{\lambda^2}{\sin 2\theta} \frac{(1 + |\cos 2\theta|)}{2} = R_P (1 + |\cos 2\theta|) \quad (1b)$$

(cf. *Internationale Tabellen*, 1935, vol. 2, pp. 562, 564). Here θ is the Bragg angle and the formulae refer to symmetrical 'surface' reflexions. If, however, the incident X-rays are completely polarized and the electric vector makes an angle φ with the normal to the plane of reflexion, then the integrated reflexions in the two cases are:

$$\varrho_{M\varphi} = R_M [\cos^2 \varphi + \sin^2 \varphi \cos^2 2\theta], \quad (2a)$$

$$\varrho_{P\varphi} = R_P [\cos^2 \varphi + \sin^2 \varphi |\cos 2\theta|]. \quad (2b)$$

Rewriting these equations in the form

$$r_M(\varphi) = \varrho_{M\varphi} / \varrho_{M\sigma} = \cos^2 \varphi + \sin^2 \varphi \cos^2 2\theta, \quad (3a)$$

$$r_P(\varphi) = \varrho_{P\varphi} / \varrho_{P\sigma} = \cos^2 \varphi + \sin^2 \varphi |\cos 2\theta|, \quad (3b)$$

where the symbol σ refers to the case when $\varphi = 0$, it is seen that, except for values of $\theta = 0^\circ, 45^\circ$ or 90° , the two functions are different, the difference being a maximum for $\theta = 30^\circ$ and 60° . Thus, it is seen that mosaic and perfect crystals differ in their behaviour with respect to polarized X-rays.

An experimental investigation was made to demonstrate this effect and to find whether it is possible to use it to assess the degree of perfection of a crystal. X-rays from the copper target of a Coolidge tube were allowed to fall on the ground (110) face of a large KCl crystal, which served as the monochromator. The 440 reflexion (Bragg angle $43^\circ 58'$) was used to give a monochromatic polarized beam.† This beam was collimated through a tube 1 mm. in diameter and 4 cm. long and was allowed to fall on the experimental crystal set at the appropriate Bragg angle. Different values of φ were obtained by rotating the goniometer, on which the crystal was mounted, about an axis coincident with the X-ray beam. The X-rays reflected by the crystal were detected by a Geiger counter. The integrated reflexion was obtained by plotting the rocking curve and finding its area. The

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† The beam will be completely polarized only if the Bragg angle of the monochromator is exactly 45° . As the Bragg angle of KCl 440 is $43^\circ 58'$, there is less than 1% of unpolarized X-rays in the incident beam. It can be shown that the maximum error arising from this in the measurement of $r(\varphi)$ is much less than the experimental errors.

voltage and current in the X-ray tube were maintained constant manually. All measurements were relative and were estimated to be accurate to about 5%.

Crystals of sodium nitrate slowly grown from a saturated solution were used in these experiments. The 633 and 422 reflexions were first studied using a natural (211) face and later after grinding the surface. The results are given in Fig. 1 in which the curves are the theoretical

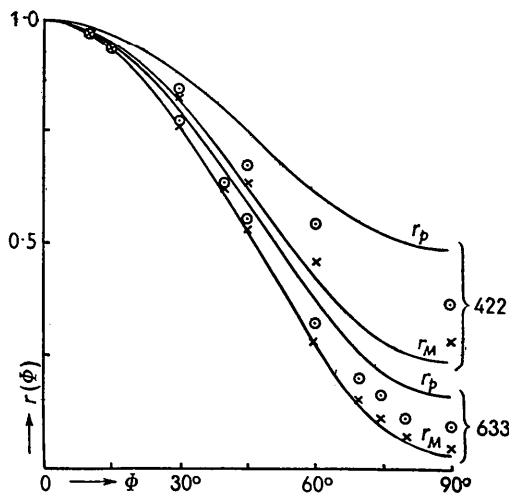


Fig. 1. Variation of integrated reflexion with azimuth of polarization. The curves marked r_P and r_M respectively are the theoretical curves for a perfect non-absorbing and for a mosaic crystal. The experimental data are indicated by the points, circles representing those obtained with a natural surface and the crosses those with a ground surface. The upper two curves and the points between them are for the 422 reflexion ($2\theta = 60^\circ 58'$) while the lower set is for the 633 reflexion ($2\theta = 99^\circ 12'$) of NaNO_3 .

curves given by equations (3a) and (3b). It may be remarked that the value of 2θ for the 422 reflexion is $60^\circ 58'$, which is very close to the value for which $r_P(\varphi) - r_M(\varphi)$ is a maximum.

In both the reflexions, one notices that the experimental points for the ground crystal are very near the theoretical curves for the mosaic crystal. However, they lie consistently above the curve, showing that the grinding has not made the crystal ideally mosaic. The data for the reflexions from the unground crystal are considerably different from those for the ground one. Thus the reflexion coefficient for perpendicular polarization ($\varphi = 90^\circ$) relative to that for parallel polarization is higher for the unground crystal than for the ground one. Therefore, if unpolarized incident X-rays are used the degree of polarization of the Bragg reflected X-rays would be higher for the ground than for the unground crystal. As far as the authors are aware, this is the first experimental demonstration of the fact that the polarization characteristic of a Bragg reflexion depends on the perfection of the crystal. This could, therefore, be used

for assessing the degree of perfection of crystals. For instance, if $r_C(\varphi)$ is the experimental value for a crystal, one may define the degree of perfection as

$$\{r_C(\varphi) - r_M(\varphi)\} / \{r_P(\varphi) - r_M(\varphi)\}.$$

This ratio is found to be approximately constant for different values of φ for NaNO_3 crystals grown from solution and has a mean value of about 0.5. An important advantage of this method of finding the degree of perfection of crystals is that the difficulty of determining absolute integrated reflexions is not present, as it requires only relative measurements for different azimuths.

It must be mentioned that the theoretical curve for $r_P(\varphi)$ relates to a perfect *non-absorbing* crystal. Preliminary theoretical studies show that, when there is a

finite absorption, the curve for $r_P(\varphi)$ departs from this, approaching that for $r_M(\varphi)$ for increasing absorptions and coinciding with the latter for large absorption coefficients. This is in agreement with the theoretical result obtained by Hirsch & Ramachandran (1950) that perfect and mosaic crystals give the same integrated reflexions when absorption is large. When the effect of finite absorption is taken into account, it is seen that the degree of perfection of the grown crystal of NaNO_3 should be higher than the value 0.5 given above. Further investigations are in progress.

Reference

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Concerning the so-called $\text{Y}(\text{OH})_3$ -type structure, and the structure of $\text{La}(\text{OH})_3$. By RUSTUM ROY and H. A. MCKINSTRY,* *School of Mineral Industries, The Pennsylvania State College, State College, Pennsylvania, U.S.A.*

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Schubert & Seitz (1946) and later Schubert & Seitz (1947) and Fricke & Seitz (1947) described the structures of the trihydrates of the rare earths, including lanthanum, neodymium, samarium, erbium and yttrium. In comprehensive papers Zachariasen (1948*a, b*) also described the structures of some of the same rare-earth hydrates, classifying them into the UCl_3 type, which structure he determined in detail. In *Structure Reports for 1947-1948* (1951) one type of structure has been classified under the name $\text{Y}(\text{OH})_3$ structure, and some 20 isotypic structures are listed, including the hydroxides and chlorides of the 4*f* and 5*f* elements. Although *Structure Reports* lists the values of Zachariasen and those of Fricke, Seitz *et al.* as though they were compatible, a glance will suffice to show that there are irreconcilable differences between the two. Thus for $\text{La}(\text{OH})_3$ Zachariasen gives $c = 3.850$, $a = 6.523 \text{ \AA}$, giving $D_X = 4.44$; whereas Fricke & Seitz give $c = 3.55$ and $a = 6.29 \text{ \AA}$, with $D_X = 5.19$. A further striking anomaly in the results of Fricke & Seitz is the fact that the unit-cell size, and hence the unit-cell volume, hardly changes at all when passing from lanthanum (121.6 \AA^3) to yttrium hydroxide (119.1 \AA^3).

Experimental

In connection with an investigation into the phase equilibrium relationships in the rare earth oxide-water systems at elevated temperatures and high water pressures it was found that single crystals (1-2 mm. long) of the various hydrates could be grown quite easily. At least four different structure types, two of them monohydrates, were recognized.

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The oxides of the elements used, La_2O_3 , Nd_2O_3 , Sm_2O_3 , Gd_2O_3 and Y_2O_3 were of 99% purity grade. However, confirmatory runs were made with material of stated 99.9% purity obtained from a different commercial source. Spectrographic examination of the 99.9% Y_2O_3 showed no impurity in excess of 0.01-0.05%. The oxides were dissolved in nitric acid, precipitated by ammonia and thoroughly washed, in order to obtain them in a reactive form. They were wrapped in platinum envelopes and heated to the desired temperature (up to a maximum of 800° C.) under the desired water vapour pressure (up to a maximum of 20,000 lb.in.⁻²) in the usual types of vessels (see Roy, Roy & Osborn, 1950) for periods from a few hours to a few weeks. The vessels were 'quenched', and the products examined by the petrographic microscope and X-ray diffraction. Powder patterns were obtained using filtered copper radiation on a G.E. XRD-3 165° spectrometer unit. The necessary oscillation, rotation and Weissenberg diagrams were obtained with unfiltered Fe, Cu or Mo radiation for the equator, first and second layer lines around the 'c' and 'a' axes.

The single-crystal data for $\text{La}(\text{OH})_3$ yielded a space group ($C6_3/m$) agreeing with that found by Zachariasen and by Fricke & Seitz. The cell dimensions obtained from these data and from the indexing of the powder pattern data, using Bunn-type charts, are given in Table 1, and the agreement with Zachariasen for $\text{La}(\text{OH})_3$ and $\text{Nd}(\text{OH})_3$ is fair. The density measured pycnometrically on a 5 g. sample was found to be $4.453 \pm 0.005 \text{ g.cm.}^{-3}$ compared with Zachariasen's X-ray density of 4.44 g.cm.^{-3} . Optical data obtained on $\text{La}(\text{OH})_3$ gave $n_e = 1.768 \pm 0.005$, $n_w = 1.740 \pm 0.005$; uniaxial positive; pronounced positive elongation. The neodymium, samarium (as also the gadolinium) hydroxides proved to be isomorphous, having the same positive elongation and very slightly higher refractive indices. Moreover, the powder patterns which are listed in Table 1 compare well among themselves and with that given by Fricke & Seitz (1947) for ' $\text{Er}(\text{OH})_3$ '. However, their unit-cell size for ' $\text{Er}(\text{OH})_3$ '