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An Investigation of the Effect of Surface Damage on the Intensity of Diffracted Neutrons

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The possible effect of surface damage on the intensity of diffracted neutrons has been investigated by a series of measurements for a plate-shaped crystal of SrF_2 with the large faces alternatively polished and roughened to various degrees. No significant effects were observed until the crystal thickness was reduced to about 1·7 mm and it is concluded that inhomogeneity of the extinction properties within the volume of the crystal is likely to be a far more important effect for normal neutron diffraction experiments.

Introduction

Recently Boehm, Prager & Barnea (1974) have published a report on X-ray diffraction measurements made on ground spherical single crystals in order to study the effect of surface damage on the diffracted intensities. Integrated intensities were measured from ground spherical single crystals of silicon, zinc sulphide and calcium fluoride before and after surface etching. These measurements showed that the surface damage of the unetched crystals gave rise to an appreciable enhancement of the strongest X-ray Bragg intensities, even in the case of zinc sulphide for which the extinction was relatively small. The effect was particularly large for calcium fluoride, for which the intensity of the 111 reflexion increased by a factor of about 38.

These results are consistent with the crystal comprising a rather perfect 'core' together with a less perfect surface 'skin', since because of their high absorption X-rays are particularly sensitive to surface effects. The nature of the surface before and after etching was confirmed by scanning electron micrographs and thus provides a possible explanation for extinction parameters which are apparently physically unrealistic, since existing considerations of extinction theory have ignored this type of inhomogeneity.

This effect could clearly be very important in X-ray diffraction measurements and these authors also suggested that a similar effect will be observed for neutron diffraction measurements. We have therefore carried out an investigation of the magnitude of this effect for neutron diffraction, although we would expect it to be much smaller in this case than for X-ray diffraction since absorption of neutrons in the sample is much less and surface effects are therefore less important.

Experimental measurements

Since neutron diffraction measurements are less sensitive to surface effects an investigation of the possible importance of surface inhomogeneity will require a choice of crystal shape having a large surface to volume ratio. In the present experiment, therefore, we have used plate-shaped crystals having two large faces suitable for various surface treatments and in addition have chosen materials for which extinction effects have been found to be particularly severe.

Of the materials examined recently at Harwell that suffering from the severest extinction has been CaF_2 (see Cooper & Rouse, 1976) and we therefore examined initially a number of plate-shaped crystals of CaF_2. However, all these were found to exhibit a large inhomogeneity within their volume, as had the crystals used in the previous study (Cooper & Rouse, 1971). Severe extinction, with a reduction of Bragg intensity of up to 80%, was also observed previously in SrF_2 (Cooper & Rouse, 1971) and we therefore next examined a plate-shaped crystal of SrF_2, which was found to be a good single crystal giving well shaped diffraction peaks with a full width at half height of 0·2°. The two large faces were fairly parallel to the crystallographic (*hhh*) planes.

The thickness of the plate was initially about 2·9 mm and a series of Bragg intensity measurements were made at a wavelength of 1·075 Å starting with the crystal polished to a 1 μm diamond finish. The large faces of the crystal were then roughened with emery paper to various degrees and the intensities remeasured. The experiment was repeated a number of times, each time starting with the large faces polished, and the thickness of the plate was reduced to about 1·7 mm before the final set of measurements. In each case *hhh* reflexions were measured with *h* between 1 and 5 for reflexion from both large faces and a number of more general *hk*0 reflexions were also measured. Repro-

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ducibility of the intensities indicated a statistical accuracy of better than 1% for the first two experiments and better than ½% for the third experiment.

Discussion

The experimental results were analysed using the Harwell *TAILS* computer program, as described previously in connexion with the earlier SrF_2 measurements (Cooper & Rouse, 1971), using the Cooper–Rouse extinction formalism (Cooper & Rouse, 1970) with calculated path lengths and absorption factors. An isotropic thermal diffuse scattering correction (Cooper & Rouse, 1968) was also applied. The values of all parameters except the effective domain radius (r^*) were taken from the analysis of the earlier measurements and only r^* and the scale factor (s) were refined.

The data were analysed initially using a homogeneous model with a single value of the effective domain radius to represent the average state of the crystal as a whole. Very good agreement was obtained for the *hhh* reflexions in all cases, with weighted reliability index (R_I^w) values of less than 2%. The overall agreement for all measured reflexions was not quite so good with R_I^w values of 4 or 5%. Because of the more straightforward geometry we have therefore examined in detail particularly the results for the *hhh* reflexions.

The effect of surface roughness is expected to manifest itself in two possible ways. The effective domain radius will be reduced for the surface layer so that the single value of this parameter which is used in a homogeneous model to represent the average state of the whole crystal may be smaller for a crystal with a roughened surface than it will be for the same crystal with a polished surface. Secondly, since the relative importance of the large surface of the plate will vary from reflexion to reflexion, depending on the precise geometry of the diffraction process, systematic deviations may occur from the predictions of the homogeneous model.

The results of the analyses of the *hhh* reflexions are therefore summarized in Table 1 where we have listed the values of the crystal thickness (t), r^*, s, R (*i.e.* R_I^w), y_{hhh} ($=y_{\bar h\bar h\bar h}$) and Δ_{hhh}, where y_{hhh} is the extinction factor multiplying the theoretical extinction-free intensity value and Δ_{hhh} is the percentage difference between the observed intensity (I_o) and the extinction corrected theoretical intensity (I_c), averaged over the corresponding hhh and $\bar h\bar h\bar h$ reflexions:

$$\Delta_{hhh}=\tfrac{1}{2}\left\{\left(\frac{I_o-I_c}{I_c}\right)_{hhh}+\left(\frac{I_o-I_c}{I_c}\right)_{\bar h\bar h\bar h}\right\}\times 100\ . \qquad (1)$$

(In no case was there any significant difference between the term for a particular *hhh* reflexion and that for corresponding $\bar h\bar h\bar h$ reflexion.)

Three separate experiments were carried out on the same crystal at different times over a period of about six months. Measurements were not made on an absolute scale so that the scale factors for the separate experiments cannot be compared directly, but the scale factors for different runs of each experiment are consistent with the decrease in volume which occurred. Experiment 1 showed a small, but rather insignificant, decrease in r^* as the surface was roughened (runs 1 to 3) but this was not reversed when the surface was repolished (run 4) and no significant changes in Δ_{hhh} were observed. Experiments 2 and 3 gave r^* values essentially identical to the initial value but do show some significant changes in Δ_{hhh}.

The diffraction geometry for the *hhh* reflexions was fairly simple with approximately symmetrical reflexion in the large face of the plate. The fraction of the diffracted neutrons which pass through the surface layer of the large face on entering or leaving the crystal can thus readily be estimated. This fraction (f) increases systematically with increasing h, having approximate values of 0·27 and 0·84 for the 111 and 555 reflexions respectively for the initial measurements (experiment 1, run 1) and 0·36 and 0·88 for the same reflexions for the final measurements (experiment 3, run 2). Values for intermediate measurements lie between these values

Table 1. *Results of analysis of the hhh reflexions*

$\sigma(r^*)=0\cdot14\times10^{-5}$ cm.

	Experiment 1				Experiment 2		Experiment 3		
	1 (polished)	2 (rough)	3 (rough)	4 (polished)	1 (polished)	2 (rough)	1 (polished)	2 (rough)	2*A* (rough)
t (mm)	2·89	2·79	2·78	2·74	2·57	~2·50	2·41	1·69	1·69
r^* (10^{-5} cm)	2·24	2·16	2·07	2·05	2·25	2·30	2·30	2·27	variable
s ($\times10^7$)	2·18	2·12	2·10	2·08	2·14	2·07	1·95	1·30	1·30
R (%)	1·38	1·50	1·31	1·67	1·74	1·79	0·88	1·96	0·87
y_{111}	0·536	0·546	0·556	0·558	0·554	0·548	0·560	0·627	0·586
y_{222}	0·876	0·880	0·885	0·885	0·883	0·880	0·885	0·907	0·892
y_{333}	0·781	0·788	0·795	0·796	0·789	0·786	0·791	0·820	0·794
y_{444}	0·457	0·465	0·474	0·476	0·465	0·460	0·466	0·492	0·457
y_{555}	0·864	0·868	0·873	0·874	0·869	0·866	0·870	0·885	0·867
Δ_{111}	2·99	3·62	2·13	2·46	1·86	−0·78	−0·34	−6·05	0·67
Δ_{222}	−0·44	0·42	0·80	1·24	2·58	0·93	−0·34	−0·59	−0·30
Δ_{333}	−1·62	−1·90	−1·52	−1·53	−0·39	0·72	−1·34	−0·57	−1·25
Δ_{444}	−1·00	−0·96	−1·33	−1·60	−2·32	0·36	1·27	5·63	0·64
Δ_{555}	−0·32	−0·92	0·06	−0·36	−1·55	−1·06	0·83	2·26	−0·26

as the crystal thickness was reduced. From the y_{hhh} values it can be seen that the two reflexions which will be most sensitive to variation in the extinction properties are the 111 and the 444 reflexions. The approximate values of the fraction f for the 444 reflexion are 0·76 and 0·82 for the initial and final measurements respectively. These values are thus over twice those for the 111 reflexion so that surface effects may therefore give rise to appreciable relative changes in Δ_{111} and Δ_{444}. Such changes are in fact observed in experiments 2 and 3, but since the measurements are not on an absolute scale these are observed as a positive change in Δ_{444} and a negative change in Δ_{111}. The values for experiment 2, for which the thickness was not reduced very much, are relatively small and it is only for experiment 3, following the larger reduction in thickness that the changes become significant.

The final set of *hhh* measurements was therefore analysed in terms of a model with a variable r^* as follows. The calculated intensity values obtained from the constant r^* model were scaled to give $\Delta_{111}=0$ and the resultant value of Δ_{444} was used with the value of y_{444} for this analysis to calculate the value of r^* which would give $\Delta_{444}=0$. These values of r^* for the 111 and 444 reflexions and the values of the fraction f were then used to calculate values of r^* for the remaining *hhh* reflexions. Corrections were applied to the intensity values to allow for the variation in r^* and the data were then re-analysed to obtain the value of r^* for the 111 reflexion which gave the best agreement. The values of r^* for the other reflexions were then recalculated and the analysis was repeated in order to avoid any errors arising from the change in the r^* values.

The results of the variable r^* analysis are given in the last column of Table 1 (experiment 3, run 2*A*) and the individual values of r^* are listed in Table 2. It can be seen that the agreement for these limited data is significantly better than that obtained with a fixed r^* value, the R value being reduced from 1·96 to 0·87%. The latter value is essentially identical to that obtained for the previous polished crystal measurement (experiment 3, run 1) and is consistent with the improved accuracy which was achieved for this last experiment. The values of Δ_{hhh} for this analysis are not significantly different from those for the previous polished crystal measurements, confirming that the observed intensity changes can be accounted for adequately be introducing a variable r^* which is a function of the path through the crystal such that it reflects the differing importance of the roughened surface layer.

Table 2. *Values of r^* as a function of h for the variable r^* model*

h	1	2	3	4	5
r^* (10^{-5} cm)	2·70	2·39	2·18	1·97	1·89

Conclusions

Although the present experiment was designed specifically to detect the effects of surface damage on the intensity of diffracted neutrons through the choice of a material which suffered from fairly severe extinction and a crystal geometry which gave a large surface to volume ratio, no significant effects were observed until the crystal thickness was reduced to about 1·7 mm. Even then the observed data could be analysed satisfactorily using a conventional homogeneous model for the extinction properties with the only significant effect being a poorer fit of the two most severely extinguished reflexions. Analysis of these data in terms of a model having an effective domain radius which is a function of the path through the crystal gave a better overall agreement confirming that this effect could be accounted for in terms of the surface damage. However, it is concluded that for normal neutron diffraction experiments it is unlikely that significant effects would be observed and that inhomogeneity of the extinction properties within the volume of the crystal is likely to be a far more important effect.

It should be emphasized that these conclusions apply particularly to crystals of the type normally used as samples in single-crystal neutron diffraction studies. These will have dimensions up to a few mm only and will have been prepared in such a way that any damaged surface layer will usually be relatively thin. However, we may note that these conclusions will not necessarily apply to large single crystals of the type used, for example, as monochromators if these have been prepared in a manner which leaves a relatively thick damaged layer on the surface. For example, Dorner (1971) has shown that such crystals may have damaged surface layers as thick as 2 mm which can therefore give rise to significant changes in the diffraction properties. However, it is well known that large crystals of this type normally exhibit considerable inhomogeneity in the mosaic properties within their volume (see, for example, Schneider, 1975) and in practice this is again likely to be more important than surface damage effects. Nevertheless, it would seem advisable always to remove any seriously damaged surface layers if they constitute a relatively large fraction of the total crystal volume.

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