crease δ so that the minimum volume which is likely to be calculated exceeds this maximum erroneous volume. A value of $\xi = 1 \cdot 10^{-9}$ was satisfactory for 48-bit word length.

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The Effect of Surface Damage on the Intensity of X-rays Diffracted by Ground Spherical Single Crystals

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Integrated intensities from ground spherical single crystals of silicon, zinc sulphide, and calcium fluoride before and after etching are compared. The surface damage of the unetched crystals, apparent on scanning electron micrographs, is shown to give rise to a very appreciable enhancement of the X-ray Bragg intensities. A possible explanation for physically unrealistic phenomenological extinction parameters reported in the literature is suggested.

Introduction

The crystalline character of abraded surfaces of flat crystals treated in various ways and the effect of such treatment on the diffracted X-ray intensity has been investigated by Gay & Hirsch (1951).

A recent multi-wavelength investigation of extinction (Prager & Barnea, 1974) has suggested that ground spherical crystals may consist of a rather perfect 'core' surrounded by a less perfect 'skin'. With such a possibility clearly raising important issues for the applicability of Zachariasen's extinction theory, in which the central assumption is one of imperfectional homogeneity of the specimen, we now report on experiments designed to test this speculation.

Experimental procedures and results

Scanning electron micrographs of a single crystal of semiconductor-quality silicon ground to spherical shape with a Bond-type grinder (Bond, 1951), whose grinding surface was impregnated with 800-mesh diamond dust, are shown in Figs. 1 and 2. Figs. 3 and 4 show micrographs of a similarly prepared sphere of silicon after brief etching in a solution consisting of 16 parts of 48% hydrofluoric acid, 44 parts of glacial acetic acid, and 100 parts of fuming nitric acid. To facilitate the microscopy, a thin layer of gold was evaporated onto both crystals. The ground crystals were rinsed vigorously in acetone before the gold was deposited. The micrographs of the unetched crystals reveal considerable surface roughness, fine cracks, and possibly some detached particles. The etched crystals are comparatively smooth; some faceting of the etched surface is apparent.

Integrated intensities of a number of Bragg reflexions of silicon were measured on a manual Picker four-circle diffractometer using nickel-filtered copper $K\alpha$ radiation detected by a scintillation counter. The measurements were carried out in the following sequence. A silicon sphere was ground and then rinsed in acetone; integrated intensities of a number of reflexions were then measured. The crystal was then detached from the glass fibre on which it was mounted, briefly etched, and remounted. The measurements were repeated with the same settings of the X-ray generator and detector electronics.

The integrated intensities of equivalent reflexions differed by no more than 4%. The peak heights of the two measured equivalent reflexions were compared with those of other equivalent reflexions and no discrepancies outside the above limits were observed.

In order to exclude the possibility that the very appreciable decrease in the intensities observed with the etched crystal was due to a peculiar intensity distribu-

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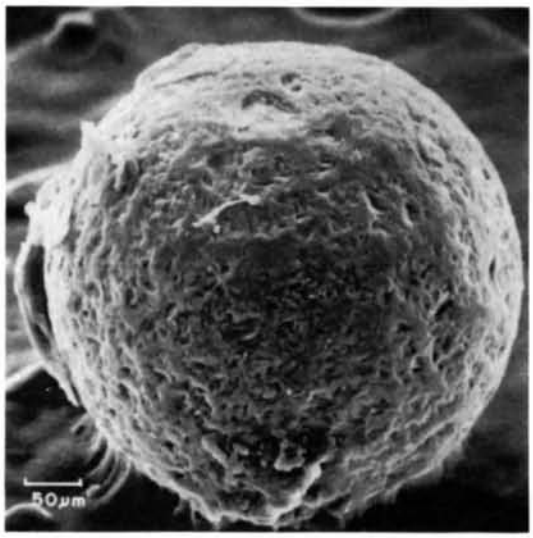

Fig. 1. Scanning electron micrograph of a ground, unetched silicon sphere.

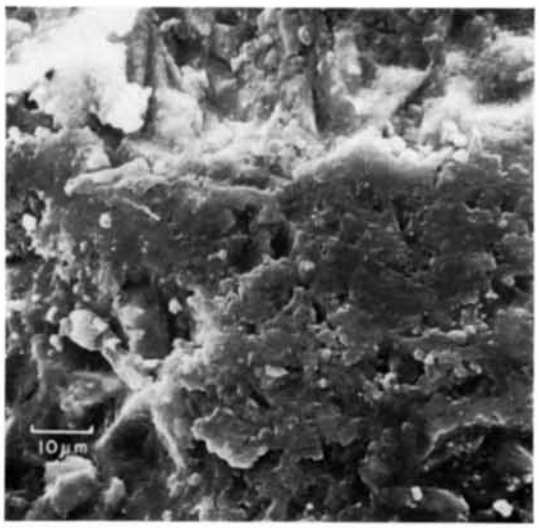

Fig. 2. The same as Fig. 1 at higher magnification.

Fig. 3. Micrograph of etched silicon sphere.

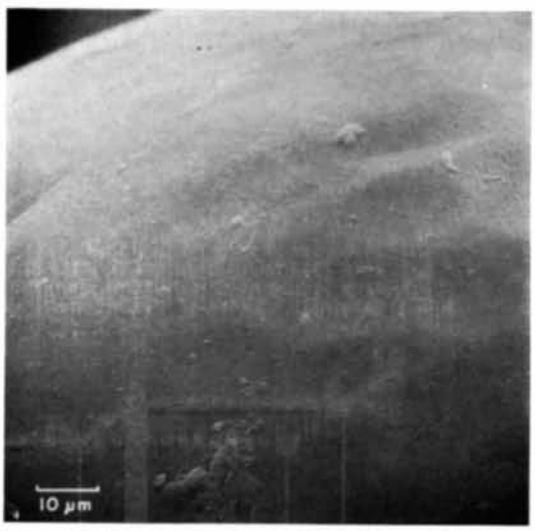

Fig. 4. The same as Fig. 3 at higher magnification.

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tion in the incident X-ray beam, the crystal was briefly reground and the intensities were remeasured and found to increase, in spite of the loss of volume of the crystal caused by the grinding. The intensities (corrected for volume and absorption) increased with increasing duration of the grinding.

The results of these measurements are summarized in Table 1. In order to make a comparison of the integrated intensities possible, the three sets of intensities, before etching, after etching and after regrinding, were multiplied by the appropriate absorption factors, obtained from *International Tables for X-ray Crystallography* (1959), and divided by the volume of the crystal.

Table 1. *A comparison of integrated intensities of a ground spherical silicon crystal before and after etching (a correction for absorption and volume differences is included)*

hkl	Integrated intensity before etching; radius of sphere, $R=0{\cdot}130$ mm	Integrated intensity after etching, $R=0{\cdot}105$ mm	Integrated intensity after regrinding, $R=0{\cdot}090$ mm
111	423594	81170	291316
400	161187	46266	102829
331	76208	26993	46898
422	93823	33092	74949
511	60037	21748	38881

It was also noted that etching resulted in a decrease in the widths of the Bragg peaks. This was to be expected, even if only on account of the decreasing size of the crystal. However, the widths increased after regrinding, thus indicating that at least in part this narrowing was due to increasing crystal perfection.

In order to test whether the effect of surface damage is restricted to rather perfect crystals such as silicon, a similar experiment was carried out with a cubic zinc sulphide (sphalerite) sample ground from mineral occurring naturally in Santander, Spain. Unlike in silicon, etching of zinc sulphide resulted in a relatively smaller decrease in the intensities and this decrease was restricted to the low-angle reflexions. Even so, removal of a 10 μm layer resulted in a loss of 25% of the 111 intensity (after correction for volume changes and absorption). This is consistent with the almost negligible extinction observed in other samples of ZnS of the same origin in measurements of Debye–Waller factors (Z. Barnea & B. Post, unpublished). Further etching caused no significant change in the corrected intensities. Indeed, the cross section of a sphere which cleaved during grinding consisted of smooth, optically transparent material surrounded by a 10-μm damaged layer.

By far the largest effect was observed in calcium fluoride. The corrected integrated intensity of the 111 reflexion of this crystal decreased by a factor of about 38 after etching in concentrated H_2SO_4 at 130 °C. Detailed results for this crystal are not presented, both on account of the preferential etching which changed the shape of the crystal and because after etching many reflexions became too weak for reliable measurement.

Concluding remarks

Evidence of the very marked effect of surface damage on the Bragg intensities of a number of ground spherical crystals has been presented. It is expected that a similar effect will be observed in the diffraction of neutrons by ground crystals. In fact, the absence of polarization would facilitate the investigation of this effect with neutrons.

A detailed and quantitative interpretation of our results is at present impossible. Theoretical treatments of extinction have hitherto always assumed homogeneity of the state of perfection throughout the crystal. It is, for instance, not clear whether Zachariasen's extinction theory (Zachariasen, 1967) could be modified to include a model wherein a relatively perfect crystal 'core' is enclosed in an imperfect 'skin'. In any case, such a theory would obviously require additional parameters describing the dimensions and states of perfection of the 'core' and 'skin' respectively.

A further difficulty is the correction of the intensities for absorption. If the scattering power is a function of the location in the crystal, then the integrated intensity is proportional to the volume integral of the scattering power corrected for absorption, and there is no conveniently separable absorption factor.

It could, of course, be argued that in the absence of a theory suitable for ground crystals exhibiting perfectional inhomogeneity, all accurate work should be carried out on etched or unground crystals (*cf.* Cahen & Ibers, 1972). However, we believe that we have clearly demonstrated the prohibitive decrease in intensity that this could in some cases entail. Moreover, while it is recognized that the application of Zachariasen's theory results in a remarkable improvement in the agreement between the observed and calculated structure factors, there is evidence that this theory cannot be applied to rather perfect crystals exhibiting very large extinction (Cooper & Rouse, 1970; Lawrence, 1972).

Experimental tests of Zachariasen's theory appear to have been carried out mostly on ground crystals (Zachariasen, 1968; Prager, 1971; Killean, Lawrence & Sharma, 1972). This may well account for the physically unrealistic values of the phenomenological extinction parameters found, for example, by the latter authors.

The inconsistency of the high crystal perfection apparent in topographs of α-oxalic acid dihydrate (Michell, Smith & Sabine, 1969) with the average perfect domain size derived from neutron intensity measurements could also have been partly or entirely due to the surface damage of the crystal used in the intensity measurements. If this were the case, then the refined average domain size would be a peculiarly weighted average reflecting the very different states of perfection of the surface and bulk of the crystal.

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Thermally Excited Forbidden Reflections*

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Methods have been developed for predicting the thermal excitation of certain structurally forbidden reflections in simple crystals. The excitation of these reflections is related to the anharmonicity and anisotropy of the atomic thermal motion. The methods are illustrated by their application to the cuprite and *A*15 structures. New extinction rules for these reflections are derived, and their structure factors are given in terms of the thermal parameters of the structures.

Introduction

The experimental observation of very weak Bragg maxima forbidden by the structure in simple crystals dates from W. H. Bragg's (1921) measurement of the 222 reflection of diamond. Early attempts to understand and interpret this anomaly in the diffraction pattern of diamond include those of Renninger (1935) and Pisharoty (1941). More recent work (Renninger, 1955; Götlicher & Wölfel, 1959; Renninger, 1960; Demarco & Weiss, 1965; and Colella & Merlini, 1966) has extended the observation to silicon and germanium and has included a determination (Roberto & Batterman, 1970) of the unusual temperature dependence of this reflection. The phenomenon is now understood to be partly due to the noncentrosymmetric electron distribution about the atomic sites in elements with the diamond structure and partly to the anharmonic character of the thermal motion in this structure. That there is a contribution to the intensity from thermal motion is evident from the neutron measurements of Keating, Nunes, Batterman & Hastings (1971). The measurements of Trucano & Batterman (1972) of the 442 reflection in silicon extend the phenomenon to the general class of structurally forbidden reflections for which h, k, and l are all even but nonzero, and $h+k+l=2(2p+1)$. Their intensity data as a function of temperature also show that the effects of electron distribution and thermal motion tend to oppose each other, leading to a characteristic temperature at which the intensity of the 442 vanishes.

In spite of the attention given to thermally excited forbidden reflections in the diamond structure, to the writer's knowledge they have not been studied in any other crystal. It is our purpose here to suggest that the phenomenon may be fairly common, to provide a basis for predicting which of the structurally forbidden Bragg maxima are excited, and to develop methods for interpreting their integrated intensities in terms of the thermal parameters of the crystal. For simplicity we will omit diffraction effects related to nonspherical atomic electron distributions, taking the atomic scattering factor to be real and isotropic in reciprocal space. The development is illustrated by its application to cuprite and the to *A*15 structure, a prototype for which is the intermetallic compound Nb_3Sn.

Forbidden reflections in cuprite

The mineral cuprite, Cu_2O, is cubic with two formula weights per cell. The space group is $Pn3m$ and there are

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