Anomalous Scattering of X-rays in Perfect Germanium Crystals

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Detailed measurements have been made of the reflected and transmitted intensities for scattering of X-rays from perfect germanium crystals for μt values from 0·6 ('thin' crystal) to 20 ('thick' crystal). Both radiation from emission lines and monochromated 'white' radiation have been used. Very good agreement with the dynamical theory of X-ray scattering was found.

Introduction

In recent years, a large number of papers have been published on the anomalous scattering of X-rays in perfect as well as defective crystals. In these experiments the integrated reflecting power, or in some cases even the full shape of the rocking-curve, has been measured for a wide range of thicknesses but only for a few standard wavelengths (*e.g.* Cu $K\alpha$ and Mo $K\alpha$). We have therefore found it worth while to measure the full angular shape of the reflected and transmitted intensities in a double-crystal spectrometer for a wide range of wavelengths on both sides of the K-absorption edge in germanium (0·63 < λ < 2·29 Å, λ_{GeK} = 1·12 Å). Crystals of thicknesses ranging from 41 μm to 183 μm were used. The product of the linear absorption coefficient μ and the crystal thickness t has values from about 0·6 up to 20, *i.e.* the interval from thin to thick crystals was covered. The corresponding theoretical curves were also calculated according to the dynamical theory of X-ray scattering and very good agreement between theory and experiment was found. The present investigation also gives valuable information about a technique that is seldom used in this context; that of a continuous range of wavelengths obtained by monochromating white radiation.

In the experiment reported here, we have found it very difficult to perform measurements in the range $\lambda < \lambda_{GeK}$ and great care had to be taken, not to get results that were far away from the theoretical prediction. No substantial difficulties were encountered for other wavelengths.

Experimental

The measurements were carried out with an X-ray double-crystal spectrometer which has been described previously (Brogren, 1951; Brogren, Efimov, Laussen & Persson, 1968). The spectrometer was used in the Bragg–Laue position. The transmitted and Laue-reflected intensities were recorded with two scintillation detectors connected to linear amplifiers and pulse height analysers. A plane-parallel germanium single crystal with the (220) planes parallel to the surface was used as the monochromator crystal. The samples were prepared from plane-parallel germanium single crystals cut for symmetric Laue reflexion. The (220) planes were perpendicular to the surface. By chemical etching with iodine etch B (Wang, 1958) thicknesses of 41, 64, 116 and 183 μm were obtained. The dislocation density was less than 100 cm^{-2}, which was checked by etch-pit counting and Lang topography. The thicknesses were determined from the transmitted radiation and the linear absorption coefficients (Grimvall & Persson, 1969).

The 13 wavelengths used were emission lines from Cr, Fe, Cu, W and Mo targets and wavelengths obtained from the continuous spectrum of a W target. The position of the monochromator crystal for every wavelength was calculated so that the same area of the analyser crystal was struck by the incident beam.

For wavelengths close to the K-absorption edge (1·117 Å) there was a strong influence of germanium K-fluorescent radiation (Brogren, Efimov & Persson, 1969a). All experimental results were corrected for this effect.

The spectral window of the beam reflected from the monochromator crystal was about 0·01 Å for the slit widths used (Brogren, Efimov & Persson, 1969b). No corrections of the results were made since the wavelengths nearest to the K-edge were 1·099 and 1·150 Å.

Results and discussion

A large amount of data has been collected, the results of which are summarized here. Further details will be published elsewhere.

In Fig. 1(*a*) and (*b*) the rocking-curves for crystal thicknesses t = 41 μm and 183 μm measured with Cu $K\alpha$ radiation are given. In Fig. 2 the maximum percentage reflexion for the transmitted and reflected beam *versus* crystal thickness is plotted for Cu $K\alpha$ radiation. In Fig.

3 the maximum percentage reflexion for the transmitted and reflected beam *versus* wavelength is plotted for $t = 64\mu$m. The values of the half widths of the rocking-curves *versus* wavelength are plotted for $t = 64$ μm in Fig. 4.

The theoretical curves have been calculated from the dynamical theory of scattering in the double-crystal case (Zachariasen, 1945; von Laue, 1960). Absorption coefficients from a previous investigation were used (Grimvall & Persson, 1969). The atomic scattering factor was taken from *International Tables for X-ray Crystallography* (1962). The real part of the anomalous contribution to the scattering factor has been calculated from the theoretical expressions of Hönl (1933) and Eisenlohr & Müller (1954). The ratio of the imaginary parts of the scattering factor for the planes H and 0 was obtained from the measured absorption coefficients (Grimvall & Persson, 1969) and the quadrupole terms of the atomic absorption cross sections as calculated by Wagenfeld (1966). A Debye–Waller factor of 0·966 was used corresponding to a Debye temperature of 291 °K (Batterman, 1964).

As can be seen in Fig. 2, the intensity of the reflected beam decreases with increasing t for a given angle of incidence. Because of the Pendellösung effect the curve should show periodic changes in intensity (Batterman & Patel, 1968). In our experiments no oscillations in the intensities were found. For a perfect plane-parallel crystal with zero absorption, the theory gives intensity variations in the Bragg–Laue reflected beam similar to those given by Zachariasen (1945) for the integrated reflexion power in the Laue case. However, in an absorbing crystal, these variations will be partly masked by a non-oscillatory contribution. A variation in the thickness of the crystal (in our case about $\pm 1·5$ μm) will also tend to average out the oscillations. When the crystal is only weakly absorbing, the normal and parallel components of the wave field are roughly of equal importance but extreme values in the intensity do not occur for the same thickness. Considering these facts, one would expect to see intensity variations at the lowest wavelengths and at wavelengths just above the K-edge. It would be easier to see the variations for the lower wavelengths since the Pendellösung period is larger there [15·1 μm for 0·709 Å (Persson, Zielińska-Rohozińska & Gerward, 1970)]. The experimental difficulties were considerable in both ranges and no attempt was made to detect the oscillations, if any. Such measurements have been performed on a three-crystal spectrometer, where it was possible to get an essentially parallel and monochromatic beam (Persson *et al.*, 1969). Even with this instrument the oscillations were apparent only up to a crystal thickness of about 60 μm. In order to make a comparison with the theoretical curves the average of the trigonometric functions which occur in the equations was taken so as to smear out the oscillations.

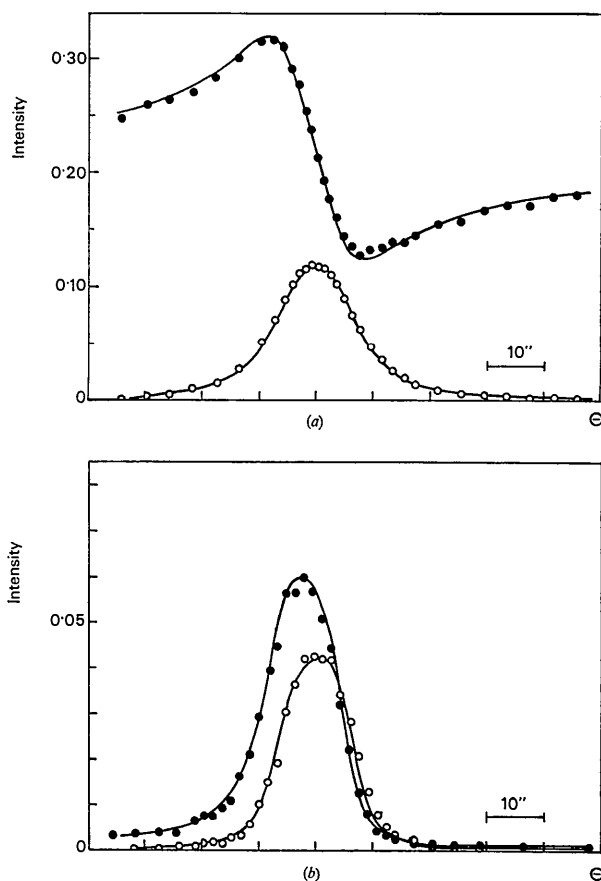The interference of wave fields can be studied not only as a function of crystal thickness at a fixed angle

Fig. 1. Transmitted and reflected intensities of Cu $K\alpha$ radiation for (a) $t = 41$ μm ($\mu t = 1·4$) and (b) $t = 183$ μm ($\mu t = 6·4$). Filled circles denote the transmitted intensity, open circles the reflected intensity and full lines the theoretical curves.
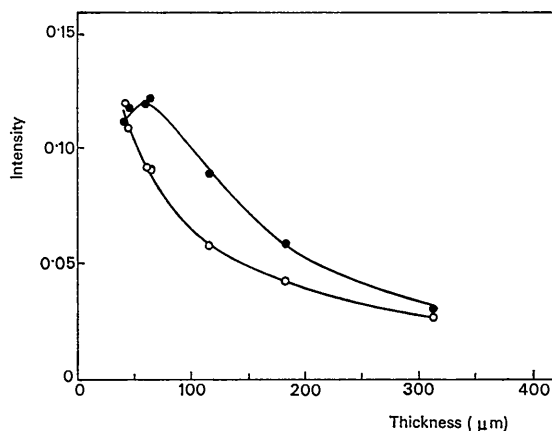

Fig. 2. The maximum percentage reflexion *versus* crystal thickness for Cu $K\alpha$ radiation. Filled circles denote the transmitted beam, open circles the reflected beam and full lines the theoretical curves. The experimental values for $t = 312$ μm are taken from Brogren (1962). By maximum transmitted intensity here is meant the difference between the actual intensity and that transmitted far from the Bragg position.

of incidence, but also as a function of this angle for a given crystal thickness. Subsidiary maxima of the rocking-curve for thin silicon single crystals have been found by some authors (Kohra & Kikuta, 1968; Kikuta & Kohra, 1968; Lefeld-Sosnowska & Malgrange, 1968). With our experimental set-up we cannot get an incident beam narrow and parallel enough for this measurement. All our rocking-curves have been smooth without subsidiary maxima.

Slight discrepancies were found between theory and experiment for the maximum percentage reflexion for the wavelengths just below the K-edge (Fig. 3) and for the half widths for the shortest wavelengths (Fig. 4). These discrepancies were present to a certain extent in all the crystals regardless of thickness. It is surprising that the maximum percentage reflexion lies above the theoretical curve instead of below it as is the case for still lower defect crystals. The agreement is good for still lower angles of incidence and also for the region of high absorption at long wavelengths. Uncertainties in the input parameters in the theoretical calculation cannot be
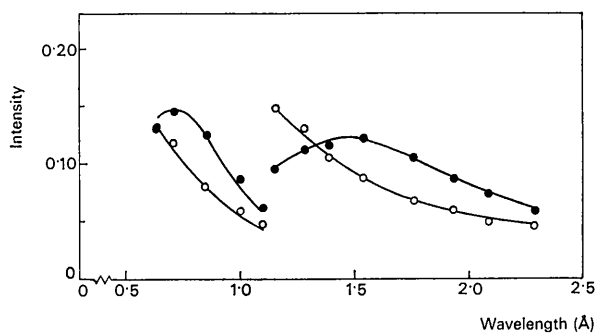

Fig. 3. The maximum percentage reflexion *versus* wavelength for $t = 64\ \mu$m. Filled circles denote the transmitted beam, open circles the reflected beam and full lines the theoretical curves. By maximum transmitted intensity here is meant the difference between the actual intensity and that transmitted far from the Bragg position.
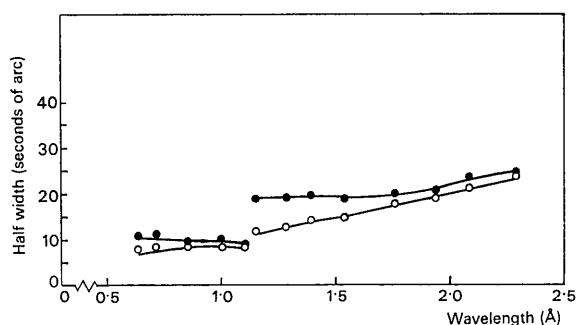

Fig. 4. Half width *versus* wavelength for $t = 64\ \mu$m. Filled circles denote the transmitted beam, open circles the reflected beam and full lines the theoretical curves. The half width for the transmitted beam refers to the part of the rocking curve that lies above the value of the intensity far from the Bragg position.

responsible for the discrepancy in the region just below the K-edge. However, the experimental difficulties in this range of wavelengths were considerable (*e.g.* fluorescent radiation) and it is doubtful if the discrepancy is of any significance.

For the shortest wavelengths, the measured half widths are somewhat larger than the theoretical ones. This may be due to difficulties that arise at small angles of incidence. It has been found that diffracted intensities are more sensitive to the imperfections of the crystal in the case of short-wavelength radiation (*e.g.* Patel, Wagner & Moss, 1962; Patel & Batterman, 1963; Ghezzi, Merlini & Pace, 1967). The influence of surface unevenness on the Bragg-reflected beam will also be larger the smaller the Bragg angle. Imperfections in the monochromator and analyser crystals and unevenness of the monochromator crystal will thus be important when short wavelengths are used. We also found that greater care had to be taken in the adjustment of the analyser crystal reflecting planes perpendicular to the beam for short wavelengths.

In a paper by Kohra, Kikuta, Annaka & Nakano (1966) it has been observed that an investigation of the full shape of the rocking-curve (instead of just the integrated reflecting power) could be of importance in the study of temperature effects. The intensity curve of the transmitted beam from a crystal with $\mu t \simeq 1$, having a maximum and a minimum, will enable a study of the temperature dependence of the absorption coefficients for each of the two present wave fields. Repeated measurements over a wide temperature range would therefore be of interest.

In conclusion, we have used both radiation from emission lines and monochromated white radiation in a detailed measurement of the reflected and transmitted intensities for scattering from perfect germanium crystals in the range from thin ($\mu t \simeq 0.6$) to thick ($\mu t \simeq 20$) crystals. We found a very good agreement with the dynamical theory of X-ray scattering, but there were considerable experimental difficulties for short wavelengths.

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The Use of a Redundant Axis in Defining the Basis of a Lattice

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The description of n-dimensional space by a basis of $(n+1)$ vectors, a_i ($i=1, \ldots, n+1$), is discussed, with particular reference to the Miller–Bravais system of indexing hexagonal crystals. It is shown that if a hyperplane with normal h makes intercepts h_i^{-1} on the a_i and a vector u has components u_i relative to the a_i, then $h \cdot u = \sum h_i u_i$ without any further restrictions on the h_i or u_i. Furthermore, it is possible to find a basis $a_i^t (i=1, \ldots, n+1)$ for reciprocal space such that $h = \sum h_i a_i^t$ is always true and indeed there are n degrees of freedom available for choosing such a basis. Criteria which may lead to a unique choice of a_i^t are discussed.

1. Introduction

Hexagonal crystals are usually described by means of the so-called Miller–Bravais 4-index system, since the 4 axes [$_H a_i$, $i=1,2,3$, and c in Fig. 1(a)] provide a symmetrical basis for the hexagonal lattice and it is possible to find a similarly symmetric basis [$_H a_i^t$, $i=1,2,3$, and c^t in Fig. 1(b)] to describe the reciprocal lattice. Although these bases are, of course, not reciprocal to one another (see *e.g.* Nicholas, 1970), they have the properties that:

(a) if the indices of a plane ($hkil$) are defined as the reciprocals of its intercepts on $_H a_i$ and c, then

$$h+k+i=0, \qquad (1)$$

and the normal to the plane is given by

$$h = h_H a_1^t + k_H a_2^t + i_H a_3^t + l c^t, \qquad (2)$$

where the magnitude of h is equal to the reciprocal of the distance of the plane from the origin; and

(b) since one of the axes is redundant, only directions [$uvtw$] having

$$u+v+t=0 \qquad (3)$$

need to be recognized (Weber, 1922), and [$uvtw$] is parallel to ($hkil$) if and only if

$$hu+kv+it+lw=0. \qquad (4)$$

The use of the redundant axes $_H a_3 (= -_H a_1 - _H a_2)$ and $_H a_3^t (= -_H a_1^t - _H a_2^t)$ is justified by the relatively simple crystallographic formulae that arise. Furthermore, Frank (1965) has shown how the hexagonal lattice and its reciprocal can be derived from four-dimensional orthogonal lattices whose obvious bases project to give $_H a_i$, c and $_H a_i^t$, c^t in three dimensions. Prior to Frank's paper, the basis of Miller–Bravais indexing seems never to have been examined with sufficient depth and rigour.

The aim of this paper is to consider the more general problem of introducing a redundant vector into the basis of any lattice, to show that a basis satisfying the analogue of equation (2) can always be found for the reciprocal lattice and indeed that this basis is not unique. The virtue of having such a relation is that the usefulness of the concept of the reciprocal lattice is

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