of $t$, because the roots – the candidate values of $u$ – are continuous functions of $v$, and indeed we have found that the optimum value of $u$ varies very slowly with $v$.

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# Temperature Effect of X-ray Diffraction Intensities for a Perfect Crystal across the Absorption Edge: Laue Case

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## Abstract

By using a Ge perfect crystal, the 422 X-ray reflection intensities have been measured across the Ge $K$ absorption edge in the Laue case. A conspicuous temperature dependence has been observed in the ratio of the integrated diffraction intensities below and above the absorption edge, which is peculiar to an absorbing perfect crystal. This temperature dependence is much larger in the Laue case than in the Bragg case.

## Introduction

When the integrated reflection intensities are measured as a function of X-ray energy, the ratio of the intensities below and above the absorption edge changes when the temperature of a perfect crystal is varied. The temperature dependence (we abbreviate it as 'the temperature effect' hereafter), which is not expected for a mosaic crystal, has been studied theoretically by Kawamura & Fukamachi (1979) and experimentally by Fukamachi, Kawamura, Hayakawa, Nakano & Koh (1982). Kawamura & Fukamachi (1979) have studied the temperature effect theoretically by using the $\bar{5}\bar{5}\bar{5}$ reflection from a GaAs(111) perfect crystal in the Bragg case as a model across the $K$ absorption edge of Ga. Fukamachi *et al.* (1982) have measured the 777 reflection intensities from InSb(111) across the In $K$ absorption edge for both a perfect and a mosaic crystal, and confirmed the temperature effect. In these two cases, the reflection intensities in the Bragg case have been studied, although a similar or larger temperature effect may be expected in the Laue case.

In the present paper, we report on the temperature effect in the Laue case by measuring 422 reflection intensities from a Ge(111) perfect-crystal face. The integrated reflection intensities are measured by energy-dispersive X-ray diffractometry with a solid-state detector (SSD) (Fukamachi, Hosoya &

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Okunuki, 1976) both at liquid-nitrogen temperature and at room temperature.

## Calculation

For discussing diffracted intensities from a perfect crystal around the absorption edge of its constituent atoms, we use a dynamical theory of X-ray diffraction with absorption effect taken into account. Basic formulae have been given by Fukamachi *et al.* (1976), although the temperature factors are neglected in the formulae. By taking account of the temperature factors in the same way as Kawamura & Fukamachi (1979), we have calculated the 422 integrated reflection intensities from a Ge perfect crystal by use of the formulae. The atomic scattering factor has been obtained from the value of Cromer & Mann (1968). The anomalous-scattering factors around the Ge $K$ absorption edge have been calculated by use of the formula of Parratt & Hempstead (1954) with the value of the oscillator density of Cromer (1965).

The calculated reflection intensities are shown in Fig. 1 for a crystal 257 μm thick. The energy range of the X-rays is $\pm 150$ eV ($1\ \text{eV} = 1{\cdot}60 \times 10^{-19}$ J) around the Ge $K$ absorption edge. The Debye–Waller factor $B$ changes from 0·0 to 0·8 Å$^2$. It is noted that the ratio of the reflection intensities below and above the absorption edge systematically changes as a function of $B$, or of the sample temperature. When the value of $B$ is 0·0 Å$^2$, the ratio is about 2:1. It becomes 100:1 when $B = 0{\cdot}8$ Å$^2$. The change of the ratio is quite conspicuous in this case. For a mosaic crystal, the ratio does not depend on the value of $B$, and is $10^{12}$:1. For comparison, the integrated reflection intensities in the Bragg case are calculated and shown in Fig. 2. The X-ray energy range around the absorption edge is the same as in Fig. 1. The ratio of the intensities below and above the absorption edge changes by varying the value of $B$ in the Bragg case, too (Kawamura & Fukamachi, 1979). But the change of the ratio is not so large in the Bragg case. The ratio is about 1·4:1 when $B = 0$ Å$^2$, and about 1·5:1 when $B = 0{\cdot}8$ Å$^2$.

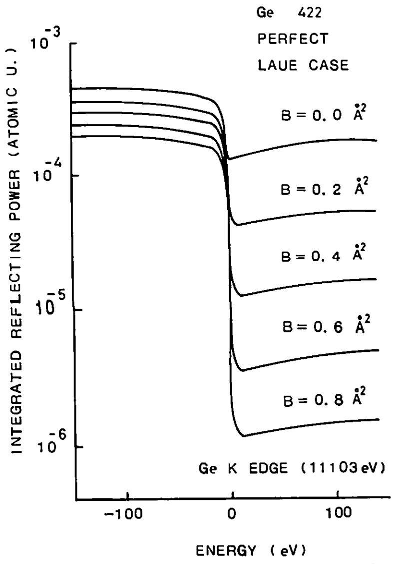

Fig. 1. Calculated values of the 422 integrated reflecting power from a Ge perfect crystal in the Laue case, in the energy range across the Ge $K$ absorption edge.

## Experiment

Since the reflection intensities in the Laue case are quite weak, it is difficult to measue the intensities by use of the conventional X-ray tube. For measuring the aforementioned change of the intensity ratio below and above the absorption edge with respect to the sample temperature, we have developed diffractometry with a rotating-anode X-ray tube and a SSD. The present system of measurement and data processing is shown in Fig. 3. The rotating-anode X-ray

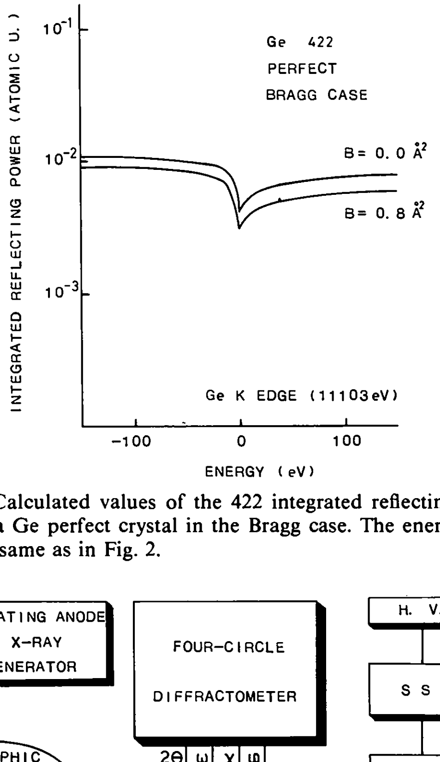

Fig. 2. Calculated values of the 422 integrated reflecting power from a Ge perfect crystal in the Bragg case. The energy range is the same as in Fig. 2.

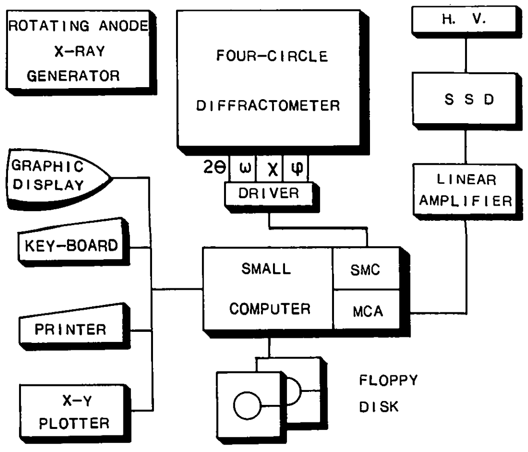

Fig. 3. System diagram of energy-dispersive diffractometry with SSD. Rotating-anode X-ray generator: JEOL JRX-12. Four-circle diffractometer: Rigaku and Huber 511. SSD: Horiba EMAX-102. Small computer: NEC PC-9801M2.

generator has a maximum power of 12 kW and is operated at 34 kV, 125 mA and with a Cu target tube. A conventional four-circle diffractometer is used. Each axis is controlled by a small computer through a stepping motor control (SMC) interface. The Si(Li) SSD is connected to a linear amplifier and a multichannel analyzer (MCA). The MCA is built in the small computer. The main memory of the small computer is 256 kbyte. Other attached equipment is shown in Fig. 3.

The optical system of the present experiment is shown in Fig. 4. The sample is a Ge(111) perfect plane crystal with no dislocation. The thickness is 257 ± 5 μm. The crystal is set at 500 mm from the X-ray source and the SSD is set at 220 mm from the crystal. For the measurement at liquid-nitrogen temperature, a cryostat is set up at the crystal position and the crystal is set in it. The energy resolution of the present optical system is about 40 eV in the energy range measured in the present experiment.

Fig. 5 shows the experimental integrated reflection intensities in the range ±250 eV around the Ge *K* absorption edge. The filled circles show the intensities at room temperature and the open circles show those at liquid-nitrogen temperature. The measuring time for each energy is 100 s. The intensities at room temperature are approximately 15 000 counts at about 250 eV below the absorption edge and 250 counts at about 200 eV above it. The intensities at liquid-nitrogen temperature are approximately 1500 counts at about 250 eV below the absorption edge and 220 counts at about 200 eV above it. The counts quoted above are the values after subtracting the background intensity. In Fig. 5, the intensities at liquid-nitrogen temperature are shifted so as to give the same value at 250 eV below the absorption edge. The decrease of the photon counts at liquid-nitrogen temperature is due to the absorption of the cryostat and liquid nitrogen. The solid lines are the calculated intensities for $B = 0{\cdot}20$ and $0{\cdot}63$ Å$^2$, which fit the experimental values at liquid-nitrogen temperature and room temperature, respectively. The intensity ratio below and above the absorption edge is about 7:1 at liquid-nitrogen temperature and about 60:1 at room temperature. The results clearly show the temperature dependence of the intensity ratio below and above the absorption edge. The fitted values of *B* in the dynamical theory of X-ray diffraction are in reasonable agreement with the reported values (Batterman & Chipman, 1962; Ludewig, 1969) within the error of the experiment.

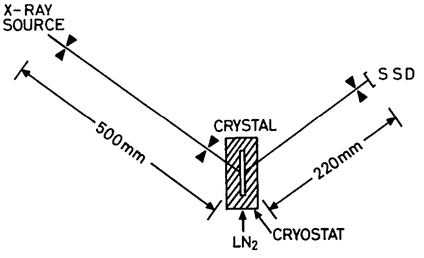

Fig. 4. Optical system of the present experiment for measuring integrated reflection intensity in the Laue case.

## Discussion

The change of intensity ratio across the absorption edge is also expected as a function of the perfection of a crystal (Datsenko, Skorokhod & Vasilkovski, 1968). In this experiment, we have used a dislocation-free perfect crystal for clarifying the temperature effect for a perfect crystal.

We have shown that the temperature effect is much larger in the Laue case than in the Bragg case. Roughly speaking, this large change is explained as follows: The reflection intensity in the Laue case depends on the absorption coefficient $\mu$ exponentially as $\exp(-\mu t)$, where $t$ is the thickness of the plane crystal. On the other hand, the intensity in the Bragg case is proportional to $1/\mu$. The absorption coefficient $\mu$ depends on the anomalous-scattering factor $f''$ linearly and the abnormal absorption part of $\mu$ in the dynamical theory depends on the temperature factor exponentially. The abnormal absorption part becomes small on increasing the value of *B* and the anomalous transmission becomes small, which results in an intensity similar to that in a mosaic crystal. Consequently, if we use a perfect crystal with an

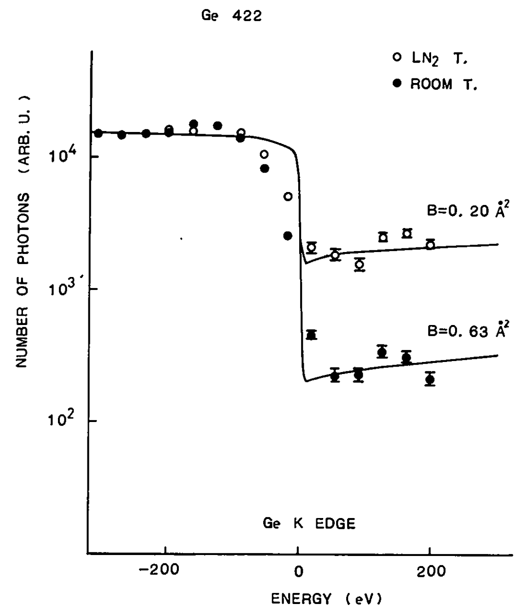

Fig. 5. Experimental results of the 422 integrated reflection intensity for a Ge perfect crystal in the symmetric Laue case across the *K* absorption edge. The open circles are the values at liquid-nitrogen temperature. The filled circles are the values at room temperature. The solid lines are the fitted curves to the experimental values at liquid-nitrogen temperature ($B = 0{\cdot}20$ Å$^2$) and at room temperature ($B = 0{\cdot}63$ Å$^2$).

appropriate thickness for measuring the reflection intensity in the Laue case, we can expect a large change in the ratio of intensity across the absorption edge as a function of the temperature factor.

Since this temperature effect is quite conspicuous, we can point out some possible applications on making use of it. For example, we can determine the temperature factor $B$ from experiment if we know the values of normal- and anomalous-scattering factors. The calculated atomic scattering factors are reliable and agree with experimental values within an error of 1%. The anomalous-scattering factors are not so reliable. Near the absorption edge, the anomalous-scattering factors depend on the surroundings of the absorbing atoms and have some fine structures corresponding to XANES (X-ray absorption near edge structure) and EXAFS (extended X-ray absorption fine structure). The values for an isolated atom calculated by the formula of Parratt & Hempstead (1954) are sometimes different from the actual values in condensed matter. However, in the energy range of more than 100 eV from the absorption edge, XANES or EXAFS does not affect very much the values of the anomalous-scattering factor. The values calculated for isolated atoms in most cases agree with experimental ones within an error of 10%. Then, if we have precise values of the anomalous-scattering factors $f'$ and $f''$, we can determine the temperature factor $B$ by use of the temperature effect. The advantage of this approach is that we need only one reflection for determination of the temperature factor. The temperature factor determined in the present experiment is $B = 0{\cdot}20$ Å$^2$ at liquid-nitrogen temperature and $B = 0{\cdot}63$ Å$^2$ at room temperature, by assuming the anomalous-scattering factors obtained for an isolated Ge atom.

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# Asymptotic Bragg Diffraction. Single-Crystal Surface-Adjoining-Layer Structure Analysis

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## Abstract

The angular dependence of the X-ray pure-diffraction intensity $I(\theta)$ has been measured in Ge and Si single crystals (surface covered with natural oxide films) by means of triple-crystal diffractometry. Measurements were extended to specimen-crystal angular deviations from the Bragg angle of up to 500 Bragg-peak half-widths. The $I(\theta)$ data at such large deviation angles are informative of both static and dynamic Debye–Waller-factor variation over crystal depth, the achievable spatial resolution turning out to be of the order of 1 nm. The high spatial resolution of the asymptotic Bragg diffraction made it necessary to consider in theory the layer-to-layer variation of both the scattering characteristics (Debye–Waller factor) and the interplanar spacings. A theoretical treatment of the problem is presented. Reconstructed Debye–Waller factors for the first four atomic planes, counting from the crystal–oxide boundary, are 0·3, 0·4, 0·7, 0·7 and 0·6, 0·6, 0·9, 1 for Ge and Si, respectively.

## 1. Introduction

X-ray diffraction methods play an important role in crystal-surface research. Triple-crystal diffractometry (TCD) is based upon a highly accurate analysis of the specimen-scattered X-ray angular distribution (the latter being measured by means of the third, *i.e.* analyzer, crystal). The TCD makes it possible to separate the purely diffractive scattering from the accompanying diffuse scattering on crystal-lattice defects

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