factors near the K absorption edges in GaAs. In these papers, we applied the dynamical theory of diffraction to an absorbing crystal. The results have shown a relatively good agreement between theoretical calculations and the experimental results in the integrated reflexion intensity curve.

The fine structures of the anomalous scattering factor, namely shoulders of $f'_{\rm Ga}(\omega)$, $f''_{\rm Ga}(\omega)$, $f'_{\rm As}(\omega)$ and $f''_{\rm As}(\omega)$ curves above respective edges are different from each other. This seems to suggest that the structures of anomalous scattering factors should be attributed to the wave functions of Ga and As, or in other words, the matrix element of the photoabsorption does not simply depend upon the density of final states in GaAs, as was discussed for GaP (Fukamachi, Shimamoto, Ohtsuki & Hosoya, 1975). It is, therefore, necessary to find better wave functions in order to discuss the anomalous scattering factors more precisely.

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References

BONSE, U. & MATERLIK, G. (1976). *Z. Phys.* **B24**, 189–191.
CLEMENTI, E. (1965). *Tables of Atomic Functions* (a supplement to the paper *IBM J. Res. Dev.* **9**, 2).
FUKAMACHI, T. (1971). *Tech. Rep. ISSP Ser. B*, No. 12, pp. 1–62.
FUKAMACHI, T. & HOSOYA, S. (1975). *Acta Cryst.* A**31**, 215–220.
FUKAMACHI, T., HOSOYA, S. KAWAMURA, T. & OKUNUKI, M. (1977). *Acta Cryst.* A**33**, 54–58.
FUKAMACHI, T., HOSOYA, S. & OKUNUKI, M. (1976*a*). *Acta Cryst.* A**32**, 104–109.
FUKAMACHI, T., HOSOYA, S. & OKUNUKI, M. (1976*b*). *Acta Cryst.* A**32**, 245–249.
FUKAMACHI, T., SHIMAMOTO, N., OHTSUKI, Y. H. & HOSOYA, S. (1975). *Acta Cryst.* A**31**, S231.
HÖNL, H. (1933*a*). *Z. Phys.* **84**, 1–16.
HÖNL, H. (1933*b*). *Ann. Phys.* (*Leipzig*), **18**, 625–655.
HOSOYA, S. (1975). *Anomalous Scattering*, edited by S. RAMASESHAN & S. C. ABRAHAMS, pp. 275–287. Copenhagen: Munksgaard.
HOSOYA, S. & FUKAMACHI, T. (1973). *J. Appl. Cryst.* **6**, 396–399.
MIYAKE, S. (1969). *X-ray Diffraction*, chapter 5, pp. 98–221 (in Japanese). Tokyo: Asakura.
UNO, R., OKANO, T. & YUKINO, K. (1970). *J. Phys. Soc. Jpn*, **28**, 437–442.

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Temperature Dependence of X-ray Reflection Intensity from an Absorbing Perfect Crystal near an Absorption Edge

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Abstract

The temperature effect of X-ray integrated reflection intensities is discussed theoretically in the energy region near the absorption edge of Ga in GaAs perfect crystal. From the calculation based on the dynamical theory of diffraction, it is concluded that the integrated intensity of $\bar{5}\bar{5}\bar{5}$ in the Bragg case shows a complicated temperature effect depending on the change of the anomalous scattering factor across the absorption edge. Calculated results are compared with a preliminary measurement, which shows a qualitative agreement with the theory.

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Introduction

The integrated reflection intensities of X-rays (IRIX) from a crystal involve the effect of anomalous scattering in the energy region near the absorption edge of the specimen atom. Cole & Stemple (1962) first pointed out that the IRIX show different variations across the absorption edge depending on perfection and polarity of the crystal. They pointed out, in particular, that the intensity ratio of hkl to its polar opposite $\bar{h}\bar{k}\bar{l}$ for a polar crystal is independent of crystal perfection. In this connection, they measured the IRIX of 111 and $\bar{1}\bar{1}\bar{1}$ for perfect and mosaic crystals of GaAs across Ga

K and As *K* absorption edges in the Bragg case, but their experimental resolution and signal-to-noise ratio were not good enough to argue the detail of the intensities in the energy region very near the edges.

Using an energy dispersive diffractometer with a solid-state detector, measurements of IRIX very near the absorption edge with much better energy resolution have been recently performed for GaAs (Fukamachi, Hosoya & Okunuki, 1976*a*,*b*; Fukamachi, Hosoya, Kawamura & Okunuki, 1977, 1979) which made it possible to compare quantitatively experiment with theoretical calculations. But in the work so far performed (except for Fukamachi, Hosoya, Kawamura & Okunuki, 1977), the temperature effect has been neglected in calculating the IRIX curves. As is well known, IRIX is proportional to $\exp(-2M)$ (M: the Debye–Waller variable) for a mosaic monatomic crystal, and to $\exp(-M)$ for a perfect non-absorbing monatomic crystal. However, a temperature effect of a more complicated nature may appear for an absorbing perfect crystal near the absorption edge. In the present paper, which is devoted to discussing the temperature dependence of IRIX for an absorbing perfect crystal, IRIX curves of the 555 and $\bar{5}\bar{5}\bar{5}$ reflections from a perfect GaAs crystal are theoretically calculated for the range near the Ga *K* absorption edge. It is revealed that anomalous temperature effects take place in the IRIX curves across the absorption edge. By a preliminary experiment, a trend predicted by the calculation was confirmed.

Theoretical basis

A theoretical basis relating to the IRIX in the symmetric Bragg case with absorption is summarized below, mainly following expressions used in an account given by Miyake (1969). The atomic unit ($\hbar = e = m = 1$) is adopted.

The energy dispersive IRIX of h reflection in the Bragg case for unpolarized X-rays is expressed by

$$R_h = (R_h^{C=1} + R_h^{C=\cos 2\theta_B})/2; \tag{1}$$

with polarized X-rays:

$$R_h^C = I_0 \frac{\omega_B C|\bar{\chi}_{hr}|}{2\sin^2\theta_B} \int P_h(W,C)\,\mathrm{d}W, \tag{2}$$

$$C = \begin{cases} 1 \text{ for perpendicular polarization} \\ |\cos 2\theta_B| \text{ for parallel polarization,} \end{cases} \tag{3}$$

where θ_B is the Bragg angle, ω_B the photon energy at the Bragg condition, I_0 the incident beam intensity and W the so-called *Selektionsfler*; $\bar{\chi}_{hr}$ is the real part of a Fourier term $\bar{\chi}_h$ representing the electron polarizability ($\times 4\pi$) at a finite temperature. $\bar{\chi}_h$ can be expressed as

$$\bar{\chi}_h = \bar{\chi}_{hr} + i\bar{\chi}_{hi}, \tag{4}$$

with

$$\begin{aligned} \bar{\chi}_{hr} &= -\frac{4\pi}{V\omega^2} \sum_j (f_j^0 + f_j') \exp(2\pi i h r_j) \exp(-B_j s_h^2) \\ &= |\bar{\chi}_{hr}| \exp(i\alpha_{hr}), \end{aligned} \tag{5}$$

$$\begin{aligned} \bar{\chi}_{hi} &= -\frac{4\pi}{V\omega^2} \sum_j f_j'' \exp(2\pi i h r_j) \exp(-B_j s_h^2) \\ &= |\bar{\chi}_{hi}| \exp(i\alpha_{hi}), \end{aligned} \tag{6}$$

where ω is the energy of the X-ray photon, V the unit-cell volume, s_h the magnitude of the scattering vector, B_j the temperature parameter, r_j the position of the jth atom in the unit cell, f_j^0 the normal part of the atomic scattering factor concerned and f_j' and f_j'' correspond to the anomalous amplitudes. $P_h(W,C)$ in (2) is a function defined by

$$\begin{aligned} P_h(W,C) &= \frac{1 + |k|^2 - 2|k|\sin\delta}{[(1-|k|^2)^2 + 4|k|^2\cos^2\delta]^{1/2}} \\ &\quad \times \{\mathscr{L}(W) + [\mathscr{L}^2(W) - 1]^{1/2}\}^{-1}, \end{aligned} \tag{7}$$

where

$$\begin{aligned} \mathscr{L}(W,C) = \{ & [(W^2 - 1 - g^2 + |k|^2)^2 + 4(gW \\ & -|k|\cos\delta)^2]^{1/2} + W^2 + g^2\} \\ & \times [(1-|k|^2)^2 + 4|k|^2\cos^2\delta]^{-1/2} \end{aligned} \tag{8}$$

$$\delta = \alpha_{hi} - \alpha_{hr}. \tag{9}$$

The quantities g and $|k|$ are given by

$$g = \chi_{0i}/(C|\bar{\chi}_{hr}|) \tag{10}$$

and

$$|k| = |\bar{\chi}_{hi}|/|\bar{\chi}_{hr}|. \tag{11}$$

The two parameters g and $|k|$ depend on temperature in general. In the following consideration related to the GaAs crystal, however, the temperature parameter $B_{\rm Ga}$ is known to be approximately equal to $B_{\rm As}$ (Uno, Okano & Yukino, 1970). In this case, therefore, as $|k|$ can be taken to be independent of temperature, g is the only parameter which is temperature dependent. g varies according to the form

$$g = \chi_{0i}\exp(Bs_h^2)/(C|\chi_{hr}|), \tag{12}$$

where χ_{hr} represents the value of $\bar{\chi}_{hr}$ at 0 K.

The values of the normal scattering factors $f_{\rm Ga}^0$ and $f_{\rm As}^0$ are calculated from atomic wave functions (Fukamachi, 1971). The values of $f_{\rm As}'$ and $f_{\rm As}''$ are obtained by an empirical formula using Cromer's (1965) values. As in a previous paper (Fukamachi, Hosoya, Kawamura & Okunuki, 1977), the imaginary part of the anomalous scattering factor $f_{\rm Ga}''$ is determined by the measurement of absorption coefficient, and the real part $f_{\rm Ga}'$ is calculated from $f_{\rm Ga}''$ using the dispersion relation (Kawamura & Fukamachi, 1978). The values of the scattering factors used for the ± 555 reflections are as follows: $f^0_{\rm Ga} = 10{\cdot}00$, $f^0_{\rm As} = 11{\cdot}21$, $f'_{\rm As} = -2{\cdot}36$ and $f''_{\rm As} = 0{\cdot}79$. The values of $f'_{\rm Ga}$ and $f''_{\rm Ga}$ are shown in Fig. 1, which is reproduced from Fig. 2 of the previous paper.

Intensity variation by change of temperature parameter near the absorption edges

1. *Behaviour of IRIX*

The solid lines in Fig. 2 indicate calculated values of the IRIX's for 555 and $\bar{5}\bar{5}\bar{5}$ of GaAs for unpolarized X-rays for $B = B_{\rm Ga} = B_{\rm As} = 0{\cdot}91$ (Uno, Okano & Yukino, 1970); the dashed lines are those calculated for $B = 0$. The IRIX's for each value of B are normalized at the highest energy range. The circles correspond to experimental values of the integrated intensities at room temperature for unpolarized X-rays (Fukamachi, Hosoya, Kawamura & Okunuki, 1977). It is seen that the forms of calculated IRIX curves are different for $B = 0$ and $0{\cdot}91$, and also that those for $B = 0{\cdot}91$ are in better agreement with experimental curves.

As for R_{555}, the calculated variations for $B = 0$ and $0{\cdot}91$ show almost a similar trend; as the X-ray energy increases, IRIX decreases rapidly in the vicinity of the absorption edge, and after marking a minimum at the edge, it shows a small gradual increase. The difference between the IRIX curves for $B = 0$ and $0{\cdot}91$ are not so appreciable in this case, but the ratio of the IRIX value below the edge point (*a*) to that above it (*b*) is definitely larger for $B = 0{\cdot}91$ than for $B = 0$.

As for $R_{\bar{5}\bar{5}\bar{5}}$, on the other hand, the IRIX curves for $B = 0$ and $B = 0{\cdot}91$ are quite different from each other. The curve of $R_{\bar{5}\bar{5}\bar{5}}$ for $B = 0{\cdot}91$ (the solid line) shows a similar trend to R_{555}, while $R_{\bar{5}\bar{5}\bar{5}}$ for $B = 0$ (the dashed line) shows a flat variation around the edge. Thus, in this case, the change in the ratio of IRIX for $B = 0{\cdot}91$ and $B = 0$ with the X-ray energy across the absorption edge is very remarkable. Incidentally, absolute values of both R_{555} and $R_{\bar{5}\bar{5}\bar{5}}$ are always larger for $B = 0$ than for $B = 0{\cdot}91$.

It should be noted that the temperature effect as seen in Fig. 2 can never appear in a mosaic crystal of GaAs. For mosaic crystals, the temperature effect reduces uniformly the magnitude of intensity by a factor of $\exp[-2M(h)]$ over the whole range of X-ray energy, so that the change in the relative intensity from below to above the edge cannot take place. The situation is also similar if the GaAs crystal were a non-absorbing perfect crystal. Therefore, the conspicuous temperature effect as seen in the IRIX curves in Fig. 2, especially that for the $\bar{5}\bar{5}\bar{5}$ reflection, should be regarded as a temperature effect which is peculiar to dynamical diffraction including absorption. In the following sections, the behavior of IRIX curves for $\bar{5}\bar{5}\bar{5}$ is specifically discussed.

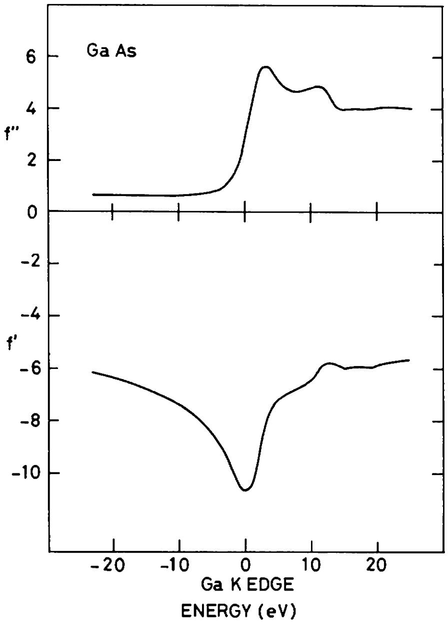

Fig. 1. The values of the anomalous scattering factors f' and f'' of Ga in GaAs crystal near the Ga K absorption edge (Fukamachi, Hosoya, Kawamura & Okunuki, 1977).

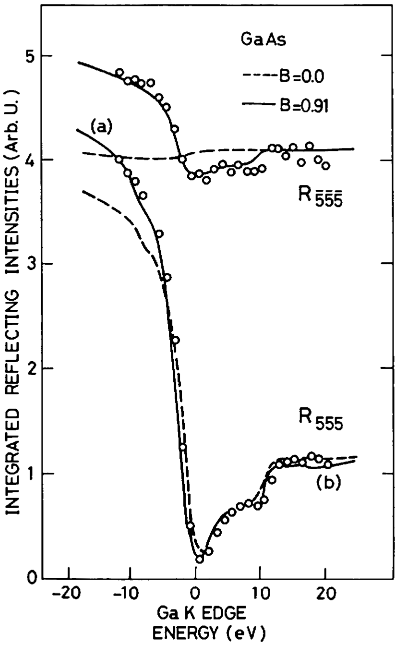

Fig. 2. The integrated reflection intensities of 555 and $\bar{5}\bar{5}\bar{5}$ from GaAs perfect crystal near the Ga K absorption edge. The solid and dashed lines are calculated values for $B = 0{\cdot}91$ and 0, respectively. The circles are experimental values at room temperature, which are normalized at the high-energy side.

2. *Origin of the temperature effect*

From (1) and (2), the IRIX for unpolarized X-rays is proportional to $|\chi_{hr}|$ and to the summation of integrals for perpendicular and parallel polarizations ($I_h^{\perp} + |\cos 2\theta_B| I_h^{\parallel}$), where

$$I_h^C = \int P_h(W,C)\,\mathrm{d}W, \quad C = \begin{cases} 1: & \perp \\ |\cos 2\theta_B|: & \parallel. \end{cases} \tag{13}$$

Since the temperature dependence of $|\chi_{hr}|$ for GaAs due to the temperature factor $\exp(-Bs_h^2)$ does not depend on the X-ray energy, the origin of the anomalous temperature effect as seen in the above should be sought in the property of the integral I_h^C given by (13). As already discussed, the quantity g is the only temperature dependent parameter included in $P_h(W,C)$ in (13) for GaAs crystals. The variation of g as a function of temperature parameter B is shown in Fig. 3 for the $\bar{5}\bar{5}\bar{5}$ reflection for X-rays of perpendicular polarization. The value of $|g|$ is larger for $B = 0{\cdot}91$ than for $B = 0$ by a factor of $\exp(0{\cdot}91 s_{555}^2)$. For the X-rays of parallel polarization, the values of $|g|$ increase further by a factor of $1/|\cos 2\theta_B|$.

In Fig. 4, variations of the integral $I_{\bar{5}\bar{5}\bar{5}}^C$ are shown for perpendicular and parallel polarizations for both $B = 0$ and $0{\cdot}91$. Difference in temperature dependence between $I_{\bar{5}\bar{5}\bar{5}}^{\perp}$ (perpendicular polarization) and $I_{\bar{5}\bar{5}\bar{5}}^{\parallel}$ (parallel polarization) near the absorption edge is due to the different values of g. For reference, the values of $|\chi_{\bar{5}\bar{5}\bar{5}r}|$ for $B = 0$ (the dot-dashed line) are also shown in Fig. 4.

In Fig. 5 are shown the $\bar{5}\bar{5}\bar{5}$ IRIX curves near the Ga K absorption edge calculated for temperature parameters $B = 0$, 1, 2, 3 and 4. The solid lines are IRIX curves for a perfect crystal and the dashed lines are those for a mosaic crystal. In this figure, the ordinate is the logarithmic scale. In the case of $B = 0$, the IRIX curve for a perfect crystal differs most appreciably from that of an ideally mosaic crystal, both in its absolute value and in its variation in the vicinity of the absorption edge. For an ideally mosaic crystal, since the value of IRIX decreases by a factor of $\exp(-2Bs^2)$, the IRIX curves keep the same shape as B varies.

On the other hand, IRIX of an absorbing perfect crystal decreases more slowly than $\exp(-2Bs^2)$ in general, although more rapidly than $\exp(-Bs^2)$. In addition, as B increases the IRIX value decreases more slowly below the absorption edge than above. Thus, the variation of IRIX of a perfect crystal on the absorption edge gradually becomes similar to that of an ideally mosaic crystal by increasing the B value or, in other words, by increasing the $|g|$ value.

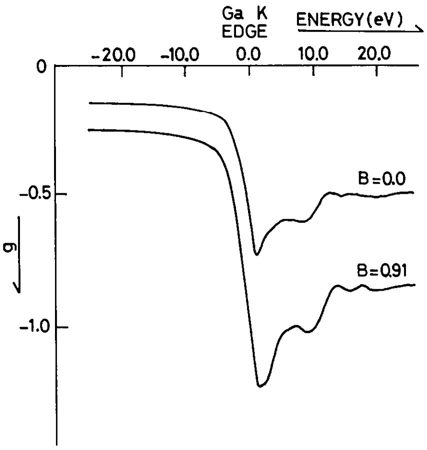

Fig. 3. The changes of g values near the Ga K absorption edge for $B = 0$ and $0{\cdot}91$ for perpendicular polarization ($C = 1$).

Preliminary experiment and concluding remark

Fig. 6 shows the result of a preliminary measurement of the IRIX curves for the $\bar{5}\bar{5}\bar{5}$ reflections from a nearly perfect crystal of GaAs at room temperature and also at liquid nitrogen temperature (Fukamachi, Kawamura & Hayakawa, 1979), where the measured value R_r for room temperature and R_{ln} for the liquid nitrogen temperature are normalized to each other at the highest range of X-ray energy. The solid and dotted curves correspond to the calculated IRIX curves for $B = 0{\cdot}91$ and $B = 0$, respectively. The behavior of the experimental curves is in good agreement with the theoretical prediction so far as it concerns the character of the ratio $R_r : R_{ln}$; that it is not uniform but varies as a

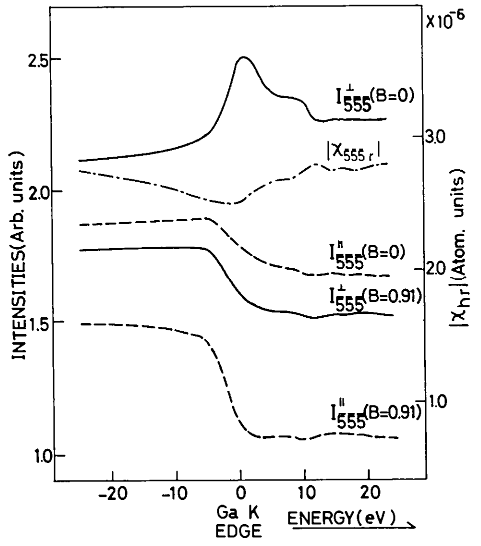

Fig. 4. Variations of the integrals of (13) for $B = 0$ and $0{\cdot}91$ near the Ga K absorption edge. $I_{\bar{5}\bar{5}\bar{5}}^{\perp}$ ($B = 0$) is that of $B = 0$ for $C = 1$ (perpendicular polarization). $I_{\bar{5}\bar{5}\bar{5}}^{\parallel}$ ($B = 0$) is that for $C = |\cos 2\theta_B|$ (parallel-polarization). The dot-dash line corresponds to the values of $|\chi_{\bar{5}\bar{5}\bar{5}r}|$ for $B = 0$.

function of X-ray energy. As fully discussed in the previous section, such a variation can be expected only for an absorbing perfect crystal. Quantitatively speaking, however, definite disagreement is seen between the experimental curves and the theoretical ones, especially relating to R_{ln}. For the present disagreement, two possibilities are at least conceivable. One is due to inaccuracy in the values of the scattering factors used in the theoretical calculation, especially those for $f'_{\rm Ga}$ in the energy range near the absorption edge. The other is the ambiguity accompanying the perfection of the crystal surface.

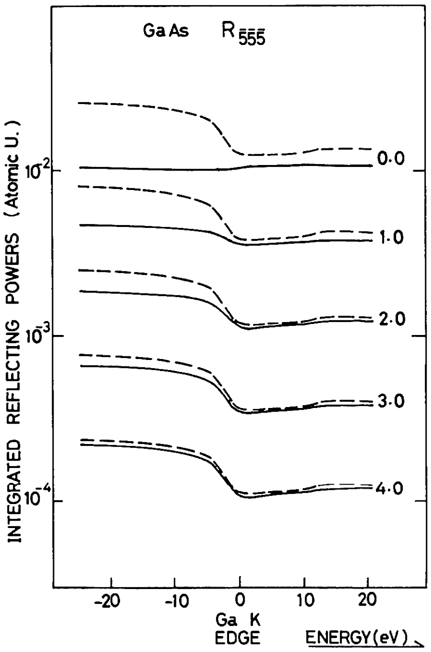

Fig. 5. Logarithmic plots of calculated $\bar{5}\bar{5}\bar{5}$ integrated reflecting powers for unpolarized X-rays near the Ga K absorption edge in absolute values. The temperature parameters are $B = 0$, 1, 2, 3 and 4. The solid lines are for a perfect crystal and the dashed lines for an ideally mosaic crystal.

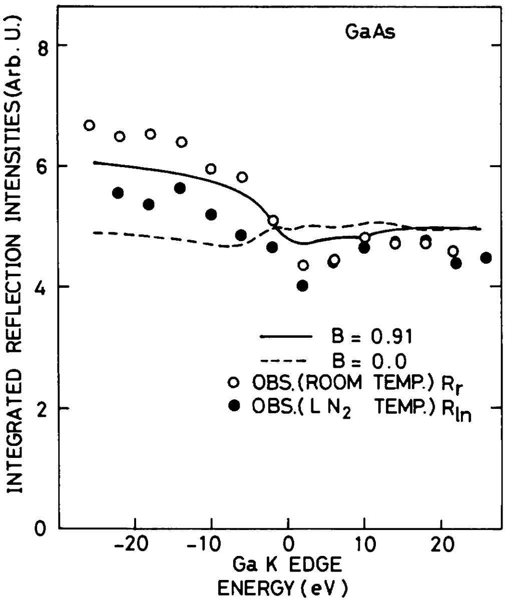

Fig. 6. Experimental values of IRIX from GaAs perfect crystal: ○: at room temperature, ●: at liquid nitrogen temperature. The solid and dashed lines are calculated values for $B = 0$ and 0·91, respectively. Each value is normalized at the high-energy range of X-rays.

More detailed study of the IRIX curves near the absorption edge is worth performing, not only in order to clarify the disagreement mentioned above but because such a study may bring us information relating to the crystal perfection, the value of the temperature parameter B, the anomalous scattering factor f' and f'', *etc.* As discussed in the previous sections, the characteristic temperature dependence of an IRIX curve for an absorbing perfect crystal is the effect which is mainly caused through the temperature dependence of the parameter g. Roughly speaking, the value of IRIX decreases as the value of $|g|$ increases. The value of g is proportional to the absorption coefficient and is generally appreciable for high-order reflections, for which the value of the normal scattering factor is small and, at the same time, the reduction of the structure factor due to the Debye–Waller factor is remarkable. Thus, the anomalous temperature dependence of the IRIX curve from an absorbing perfect crystal may appear most conspicuously for high-order reflections in the strongly absorbing energy range containing an absorption edge. This is the case for the ±555 reflections of GaAs. For more quantitative discussion, however, it is desirable to perform an experimental and theoretical study for a monatomic perfect crystal such as Ge.

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References

Cole, H. & Stemple, N. R. (1962). *J. Appl. Phys.* **33**, 2227–2233.

Cromer, D. T. (1965). *Acta Cryst.* **18**, 17–23.

Fukamachi, T. (1971). *Tech. Rep. ISSP Ser. B*, No. 12, 1–62.

Fukamachi, T., Hosoya, S., Kawamura, T. & Okunuki, M. (1977). *Acta Cryst.* A**33**, 54–58.

Fukamachi, T., Hosoya, S., Kawamura, T. & Okunuki, M. (1979). *Acta Cryst.* A**35**, 828–831.

Fukamachi, T., Hosoya, S. & Okunuki, M. (1976*a*). *Acta Cryst.* A**32**, 104–109.

Fukamachi, T., Hosoya, S. & Okunuki, M. (1976*b*). *Acta Cryst.* A**32**, 245–249.

Fukamachi, T., Kawamura, T. & Hayakawa, K. (1979). In preparation.

Kawamura, T. & Fukamachi, T. (1978). *Jpn J. Appl. Phys.* **17**, Suppl. 2, 224.

Miyake, S. (1969). *X-ray Diffraction.* (In Japanese.) Tokyo, Japan: Asakura.

Uno, R., Okano, T. & Yukino, K. (1970). *J. Phys. Soc. Jpn*, **28**, 437–442.