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X-ray Intensity Measurements on Large Crystals by Energy-Dispersive Diffractometry. II. Energy Dependences of the Friedel Pair Intensities and Their Ratio near the Absorption Edge

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It has experimentally and theoretically been confirmed that the intensity ratio $r_{\mathbf{h}}$ of Friedel pair reflexions $\mathbf{h}$ and $\bar{\mathbf{h}}$ is given by $|F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2$ in a perfect crystal as well as in a mosaic crystal both in the symmetrical Bragg case and in the symmetrical Laue case. The measurements have been carried out on a nearly perfect GaAs crystal plate in the energy range near the As K absorption edge by the use of the energy-dispersive diffractometer and continuous radiation. These results have shown a reasonable agreement with the relevant theoretical curves. The limitation of the above relation in the presence of extinction effects has been considered.

Introduction

For an ideally mosaic crystal satisfying the kinematical theory of diffraction, the integrated reflecting power is naturally proportional to $|F_{\mathbf{h}}|^2$, where $F_{\mathbf{h}}$ is a structure factor, and the $|F_{\mathbf{h}}|$ value can readily be measured on the relevant sample. In the other ideal case of a perfect crystal 'without absorption', though it cannot be a real entity, there is a definite formula by which the value of its $|F_{\mathbf{h}}|$ can be obtained from measurements. However, it is not possible to separate $|F_{\mathbf{h}}|$ from the measured integrated reflecting power by the use of the dynamical theory with absorption taken into account, as is seen from the formula (I·26) [the prefix I denotes equations of Part I of this series (Fukamachi, Hosoya & Okunuki, 1976)].

Based on the dynamical theory of Zachariasen (1945), Cole & Stemple (1962) stressed in a more detailed way that the intensity ratio between Friedel pair reflexions is given by the formula

$$r_{\mathbf{h}}=|F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2, \qquad (1)$$

even for a perfect crystal with absorption – at least in the symmetrical Bragg case. Later Holloway (1969) experimentally confirmed this Cole–Stemple relation (1) for nearly perfect crystals of GaSb and InAs by Cu and Cr $K\alpha$ radiations in the symmetrical Bragg case. This measurement was carried out with single-crystal angle-dispersive diffractometry. In the present work, the relation (1) has been confirmed more extensively for GaAs in the energy region near the As K absorption edge by energy-dispersive diffractometry. Moreover, it has been experimentally found that this relation also holds in the symmetrical Laue case on a perfect crystal plate, and this has been explained by the use of dynamical theory for a perfect crystal with absorption described by Miyake (1969). This situation is very favourable for any work for which $r_{\mathbf{h}}$ values are used (Hosoya, 1975).

Theoretical considerations

Intensity ratio in the symmetrical Laue case

From (I.26) and (I.22), the integrated reflexion power $R_{\mathbf{h}}$ for a perfect crystal in the symmetrical Laue case is given by

$$R_{\mathbf{h}}=(\omega_B C|\varphi_{\mathbf{h}r}|)/(2\sin^2\theta_B)\int P_{\mathbf{h}}(W,C)\mathrm{d}W \qquad (2)$$

$$\begin{aligned}&=\{(\omega_B C|\varphi_{\mathbf{h}r}|)/(2\sin^2\theta_B)\}\\ &\quad\times\exp\{-\mu(\omega_B)H\}\,(1+|k|^2-2|k|\sin\delta)\\ &\quad\times\int[\sin^2\{s(C)H\,\mathrm{Re}\sqrt{L(W)}\}\\ &\quad+\sinh^2\{s(C)H\,\mathrm{Im}\sqrt{L(W)}\}]/|\sqrt{L(W)}|^2\mathrm{d}W, \qquad (3)\end{aligned}$$

where C is the usual expression of polarization, and $L(W)$ (and therefore the integral) is independent of the polarity of a crystal. Thus the intensity ratio $r_{\mathbf{h}}$ between Friedel pair reflexions is simply given by

$$\begin{aligned}r_{\mathbf{h}}&=R_{\mathbf{h}}/R_{\bar{\mathbf{h}}}\\ &=(1+|k|^2-2|k|\sin\delta)/(1+|k|^2+2|k|\sin\delta), \qquad (4)\end{aligned}$$

which is already given by Cole & Stemple (1962) in the Bragg case for the usual angle-dispersive diffractometry. With the relation (I.10), the formula (4) is expressed as

$$r_{\mathbf{h}}=|\varphi_{\mathbf{h}}|^2/|\varphi_{\bar{\mathbf{h}}}|^2=|F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2, \qquad (5)$$

which is a trivial relation for a mosaic model. This relation (5) holds not only for the integrated reflecting power but also for the intensity profile at each angle or energy value. Namely because of (I.26),

$$r_{\mathbf{h}}=P_{\mathbf{h}}(W,C)/P_{\bar{\mathbf{h}}}(W,C)=|F_{\mathbf{h}}|^2/|F_{\bar{\mathbf{h}}}|^2, \qquad (6)$$

as shown in Fig. 1. The function $P(W,C)$ is given by (3), where the oscillating term $\sin^2\{s(C)H\,\mathrm{Re}\sqrt{L(W)}\}$ is included. If this rapidly vibrating term is averaged, then:

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$$\overline{P_{\mathbf{h}}(W,C)}=(\tfrac{1}{4})\,(1+|k|^2-2|k|\sin\delta)\exp\{-\mu(\omega_B)H\}$$
$$\times[\exp\{2s(C)H\,\mathrm{Re}\,\sqrt{L(W)}\}$$
$$+\exp\{-2s(C)H\,\mathrm{Im}\,\sqrt{L(W)}\}]/|\sqrt{L(W)}|^2 \tag{7}$$

holds where the first term in brackets increases with H, the thickness of a sample. Therefore, the diffraction intensity from a perfect crystal is fairly strong compared with a mosaic model, even in the region with high absorption. This situation can be seen from Fig. 7 in paper I. It is noted here that the relation (6) also holds for $\overline{P_{\mathbf{h}}(W,C)}/\overline{P_{\bar{\mathbf{h}}}(W,C)}$.

When the incident white radiation is not polarized, (4) and therefore (5) hold because of (I.23). Moreover, when it is partially polarized, the relation (5) or (6) still holds. Because the proof is similar, it is shown only for (5). Namely:

$$[R_{\mathbf{h}}(C_i)/R_{\bar{\mathbf{h}}}(C_i)]_{\text{for any } C_i}=\sum_{i=1}^{n}R_{\mathbf{h}}(C_i)/\sum_{i=1}^{n}R_{\bar{\mathbf{h}}}(C_i)$$
$$=R_{\mathbf{h}}{}^{\text{total}}/R_{\bar{\mathbf{h}}}{}^{\text{total}}=r_{\mathbf{h}}\,, \tag{8}$$

where C_i denotes either value of the two corresponding to polarization. This relation also holds in the Bragg case described later.

Let us consider the case where the absorption is neglected. Because $\mu=0$ and $f''=0$, $\varphi_{\mathbf{hi}}=0$ in (I.4). Therefore, $g=0$ and $k=0$, then the integrated reflecting power is given by (3) as:

$$R_{\mathbf{h}}=(\omega_B C|\varphi_{\mathbf{hr}}|/2\sin^2\theta_B)$$
$$\times\int[\sin^2\{s(C)H\sqrt{1+W^2}\}/(1+W^2)]\mathrm{d}W \tag{9}$$
$$=(\omega_B C|\varphi_{\mathbf{hr}}|/2\sin^2\theta_B)\pi\sum_{n=0}^{\infty}J_{2n+1}\{2s(C)H\}\,, \tag{10}$$

where J is the Bessel function. Because $|\varphi_{\mathbf{hr}}|$ is always equal to $|\varphi_{\bar{\mathbf{h}}\mathbf{r}}|$ as seen from the definition (I.3),

$$r_{\mathbf{h}}=R_{\mathbf{h}}/R_{\bar{\mathbf{h}}}=1\,. \tag{11}$$

In other words, the assumption that absorption or f'' is negligible leads readily to the validity of Friedel's law when only f' is finite. This is the case with the relevant crystal in the energy region far lower than the edge. Equation (11) also holds for a mosaic crystal without absorption in the scheme of the kinematical theory, this having no contradiction. If absorption exists at all, equation (5) also holds for a perfect crystal.

Intensity ratio in the symmetrical Bragg case for a half-infinite crystal

As referred to in paper I, the case in the title has been studied already by Cole & Stemple (1962) and Holloway (1969), though less extensively. Therefore, only a brief comment is made here. The integrated reflexion power is obtained from (I.22) and (I.24) as follows:

$$R_{\mathbf{h}}=\frac{\omega_B C|\varphi_{\mathbf{hr}}|}{2\sin^2\theta_B}\cdot\frac{1+|k|^2-2|k|\sin\delta}{[(1-|k|^2)^2+4|k|^2\cos^2\delta]^{1/2}}$$
$$\times\int[\mathscr{L}(W)+\{\mathscr{L}^2(W)-1\}^{1/2}]^{-1}\mathrm{d}W\,, \tag{12}$$

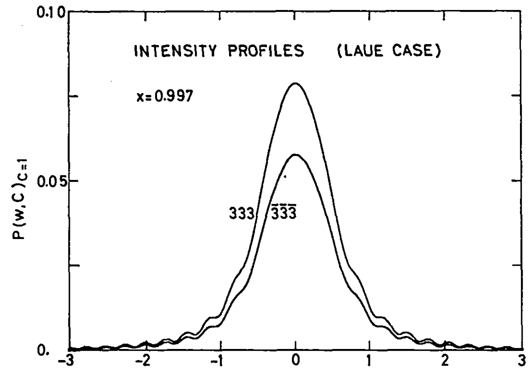

Fig. 1. Intensity profiles of 333 Friedel pair reflexions from GaAs in the Laue case calculated by (I.26). The centre of these profiles corresponds to $X=\omega/\omega_{\text{AsK}}=0{\cdot}997$; other parameters are: $g=-0{\cdot}202$, $k=0{\cdot}171$, $\delta=0{\cdot}480$ (in rad.) $\mu(\omega_B)H=5{\cdot}38$ and $s(C)H=13{\cdot}3$.

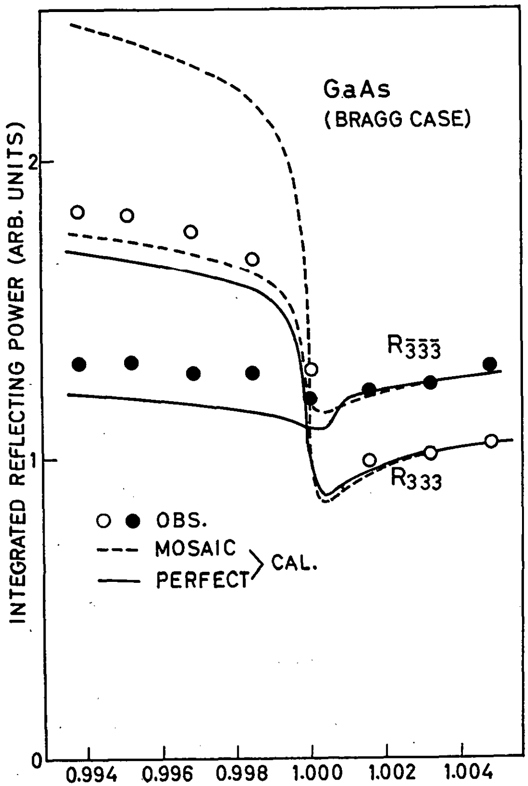

Fig. 2. Energy dependences of 333 and $\bar{3}\bar{3}\bar{3}$ reflexion intensities near the As K absorption edge. The calculated values for a mosaic crystal are scaled in the region where $X>1{\cdot}0$. The energy resolution of these measurements is ± 12 eV.

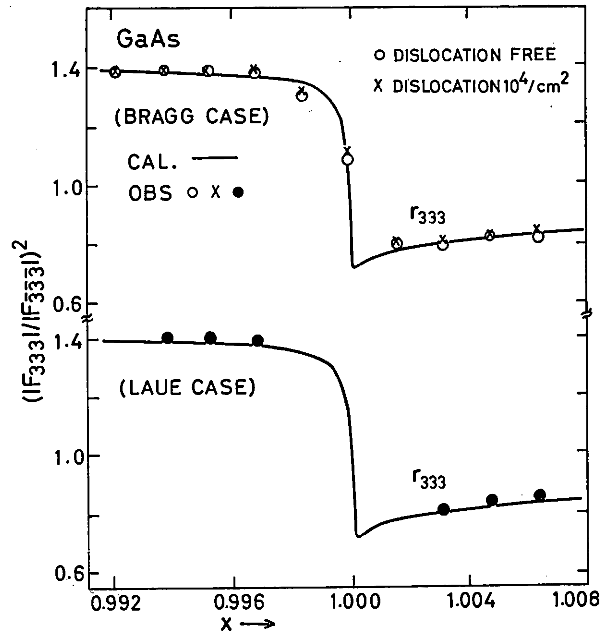

Fig. 3. Energy dependences of intensity ratios between 333 Friedel pair reflexions from GaAs in the energy region near the As K edge in both Bragg and Laue cases. The energy resolution is ± 12 eV.

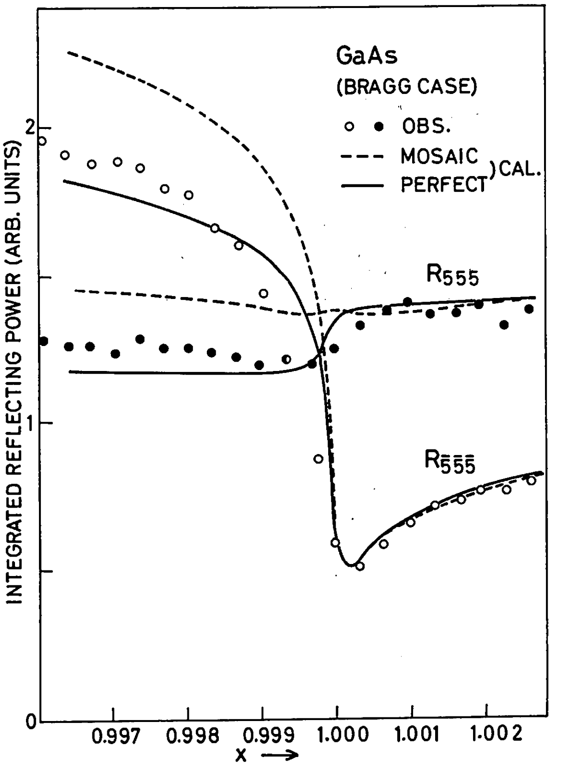

Fig. 4. Energy dependences of intensities of diffraction 555 and $\bar{5}\bar{5}\bar{5}$ near the As K edge. The measured values were obtained from a nearly perfect crystal, and the calculated values are from an ideally perfect crystal and from a mosaic crystal. The energy resolution is ± 5 eV.

where $\mathscr{L}(W)$ and therefore the integral in (12) do not depend upon the polarity. Thus:

$$r_h = R_h/R_{\bar{h}} = (1+|k|^2-2|k|\sin\delta)/(1+|k|^2+2|k|\sin\delta) = |F_h|^2/|F_{\bar{h}}|^2, \qquad (13)$$

which is identical with (4) derived in the symmetrical Laue case. Moreover, the equation (13) holds not only for integrated reflecting power but also for the diffraction profile $P_h(W)/P_{\bar{h}}(W)$, and moreover holds whether the polarization is uniform or partial, as was mentioned in the Laue case.

Measurements

The diffraction intensity has been measured on a GaAs single crystal plate in the energy region near the As K absorption edge by the method described in paper I.

333 *Friedel pair reflexions*

Bragg case

In the Bragg case, the specimen crystal used is as thick as 1 mm with (111) surfaces, and the surface was adequately treated. One sample was free from dislocation as far as observed by the etch-pit technique as was described in Part I, and the other had a dislocation density of 10^4 cm^{-2}. However, these two showed a very good agreement in intensity change near the edge. Therefore, only the results on a dislocation-free specimen are shown in Fig. 2. The scaling of the data has been carried out so that the measured values agree with the calculated data in the region where the energy is higher than the edge.

Fig. 2 shows that the measured specimen is expressed by a perfect-crystal model far better than by an ideally mosaic model, which is reasonable from the experimental facts. The intensity ratios obtained from these data are shown in the upper part of Fig. 3, where the results for both specimens are shown. The ratios between experimental and theoretical values agree.

Laue case

In the Laue case, a (110) plate about 30 μm thick has been used. The crystal is as perfect as nearly dislocation-free. The surface etching could not be carried out so well as in the case of (111) surfaces.

Fig. 7 of paper I shows the measured values of intensity change which are our concern. It shows that the change, including that near the edge, agrees well with the calculated curves based on a perfect crystal model. From these data, the intensity ratio is obtained as shown in Fig. 3 (solid circles). The theoretical curves relevant to both ideally mosaic and ideally perfect models can explain the measured values rather well. However, the ratio values very near the edge are not shown for $x = 0{\cdot}998 \sim 1{\cdot}002$, because the intensities change too abruptly there, as shown in paper I, and give unreliable ratio values.

555 Friedel pair reflexions
Bragg case

If one wishes to check the agreement between theory and experiment more precisely, it is necessary to study reflexions which can give intensity ratios differing from unity. In this sense, the 555 pair reflexions proved by the preliminary measurement to be more appropriate than the 333 pair. However, the intensity is so weak in 555 compared with 333 that only the Bragg case was feasibly measured. The specimen used was the dislocation-free crystal.

The results are shown in Fig. 4, where the scaling has been done on $\overline{555}$ as before. In this case, the specimen is considered to be a perfect crystal rather than ideally mosaic. As was shown in paper I, the difference between perfect and mosaic crystals becomes smaller for reflexions with weak intensity; in fact, 555 pair reflexions show a smaller difference than the 333 pair. In Fig. 5, the intensity ratio is shown: the agreement is again fairly good, although it is somewhat worse than in the 333 pair. This may be because the anomalous scattering factors used for calculations are not good enough in the region near the absorption edge.

Discussion

The intensity ratio of the Friedel pair reflexions from a perfect crystal is the same as that from an ideally mosaic crystal, as Holloway (1969) reported only in the Bragg case using Cu and Cr $K\alpha$ characteristic X-rays. The present work confirmed this fact more clearly and systematically by the use of continuous X-rays in both the Bragg and the Laue cases. In addition, theoretical considerations have also been extended substantially. However, so far only the symmetrical reflexion cases have been considered. Naturally it is interesting to see whether this Cole–Stemple relation also holds in asymmetrical cases. This is a problem to be studied in the future.

Cole & Stemple (1962) anticipated that the effect of polarity is independent of perfection, provided each face exhibits essentially the same degree of perfection. This implies that the extinction does not affect the value of the ratio $r_{\mathbf{h}}$. If this is valid, the situation is very favourable for various applications (Hosoya, 1975). Therefore, the preliminary consideration on extinction effects is described as follows.

Influence of secondary extinction

As is well known, the apparent absorption coefficient increases due to secondary extinction have been expressed by

$$\mu=\mu_0+gQ_{\mathbf{h}}\,, \qquad (14)$$

since early days. The value of g depends upon the mosaic structure of each sample. According to the calculation with a polarization factor taken into account, the integrated reflecting power for the Laue case with secondary extinction is expressed by

$$R'_{\mathbf{h}}=(HQ_{\mathbf{h}}/\cos\theta_B)\exp\{-(\mu_0+g'Q_{\mathbf{h}})H/\cos\theta_B\}\,, \qquad (15)$$

where

$$g'=2g(1+\cos^4 2\theta_B)/(1+\cos^2 2\theta_B)^2, \qquad (16)$$

as is given by (13*b*) in the paper by Zachariasen (1963). (The use of g and g' for the present meaning is limited

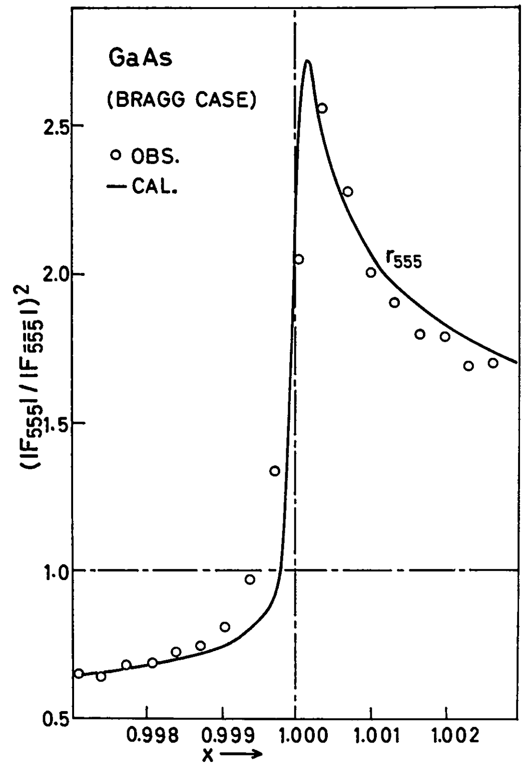

Fig. 5. Energy dependences of intensity ratio between 555 Friedel pair reflexions in the Bragg case. Open circles show the values measured on a nearly perfect crystal. The energy resolution is ± 5 eV. The solid line is calculated by (13).

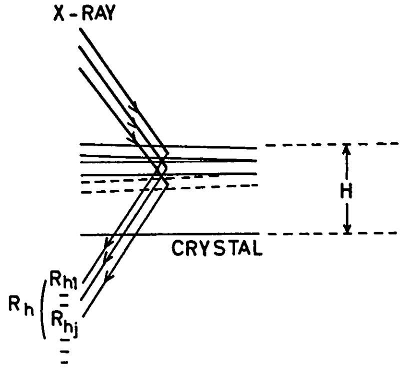

Fig. 6. A schematic view of crystal texture subject to the primary extinction only: each thin crystal plate is perfect and many plates are oriented so dispersively that the X-rays diffracted by each plate are hardly affected by other plates, without being subject to secondary extinction.

to this section.) Because of (I.18) the corresponding ratio value is given by

$$r'_{\mathbf{h}}=R'_{\mathbf{h}}/R_{\bar{\mathbf{h}}}'=r_{\mathbf{h}}\exp\{g'(Q_{\bar{\mathbf{h}}}-Q_{\mathbf{h}})H/\cos\theta_B\}\,. \quad (17)$$

The formula (17) implies that $r'_{\mathbf{h}}$ is larger than $r_{\mathbf{h}}$ for an ideally mosaic case if $|F_{\bar{\mathbf{h}}}|^2>|F_{\mathbf{h}}|^2$, while $r'_{\mathbf{h}}$ is smaller if $|F_{\bar{\mathbf{h}}}|^2<|F_{\mathbf{h}}|^2$. Thus the prediction of Cole & Stemple (1962) does not hold, at least in the case where secondary extinction exists. In the Bragg case, the relation (1) does not hold either, as is easily shown.

Influence of primary extinction

Here the Bragg case is not considered, because it is difficult to deal with a crystal plate of finite thickness with absorption by the dynamical theory.

Although it is an unrealistic assumption, let us consider the crystal with primary extinction only; for instance, a schematic model will be such a crystal as shown in Fig. 6. Then the X-rays reflected from each layer do not interfere with each other, and a pair of integrated reflecting powers, $R_{\mathbf{h}j}$ and $R_{\bar{\mathbf{h}}j}$, from the jth layer satisfy the relation (6). Therefore, the following relation holds:

$$r_{\mathbf{h}}=\frac{R_{\mathbf{h}1}}{R_{\bar{\mathbf{h}}1}}=\ldots=\frac{R_{\mathbf{h}j}}{R_{\bar{\mathbf{h}}j}}=\ldots=\frac{\sum\limits_j R_{\mathbf{h}j}}{\sum\limits_j R_{\bar{\mathbf{h}}j}}$$

$$=\frac{R_{\mathbf{h}}}{R_{\bar{\mathbf{h}}}}=\frac{|F_{\mathbf{h}}|^2}{|F_{\bar{\mathbf{h}}}|^2}\,. \quad (18)$$

This holds for both the perpendicular and parallel components of $P_{\mathbf{h}}$ or $R_{\mathbf{h}}$. Thus the relation (1) holds for a crystal with primary extinction only.

Contrary to the prediction of Cole & Stemple (1962), the relation (1) does not hold for a crystal, at least one with secondary extinction. In the present work, a nearly perfect crystal has been measured, which is probably subject to primary but not secondary extinction. This is why the experimental results show a good agreement with the calculated relation (1).

The present results for Friedel pair reflexions can be applied to a Bijvoet pair if the shape of a crystal satisfies the relevant symmetry.

In part III of the present series, measurements by the new method [(Fukamachi & Hosoya, 1975) using relation (1)] on the anomalous scattering factors of Ga and As atoms in the nearly-perfect GaAs sample in the energy region near the As K absorption edge will be reported.

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