

- (c) In the tables the number and the percentage of the correct quartets are given above the corresponding values of the arguments of the hyperbolic tangent. This is quite clear for Giacobazzo's approach. For Hauptman's approach the value of the argument of the hyperbolic tangent corresponding to the value P_+ given by (3.13) is easily derivable from the equivalence

$$P_+ = \frac{1}{2} + \frac{1}{2} \tanh(\arg).$$

The tables suggests that both methods are able to give a good measure of the reliability of the quartets, but they seem to be not equivalent. In Tables 3 and 4, for example, 9679 and 2812 quartets respectively have probability values larger than 0.69 (or smaller than 0.31), when Giacobazzo's formulae are used. The corresponding number of quartets whose probability values, according to Hauptman & Green's formulation, is larger than 0.69 (or smaller than 0.31) is 19999 and 11204 respectively. Also different are the percentages of correct relations calculated by the two approaches.

In accordance with the preceding paragraphs, we conclude that the two procedures both seem useful in procedures for crystal structure solution.

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X-Ray Intensity Measurements on Large Crystals by Energy-Dispersive Diffractometry.

III. Fine Structures of Integrated Intensities and Anomalous Scattering Factors near the K Absorption Edges in GaAs

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The anomalous scattering factor $f' + if''$ of GaAs very near the K absorption edges has been investigated with the stress on the following two points. One is the determination of f' from the measured f'' values through the linear absorption coefficient by calculation with the dispersion relation. The other concerns the effect of fine structures in the anomalous scattering factor on the integrated reflexion powers R_{555} and $R_{\bar{5}\bar{5}\bar{5}}$ in the two ranges of ± 20 eV near the Ga K and As K absorption edges. The agreement between these calculations and measurements of R values is fairly good; this fact justifies the application of the dispersion relation to the determination of the f' values near the edge. Some advantages of this application are pointed out in terms of, particularly, the phase determination of reflexions from crystals with unknown structures.

Introduction

In Part I (Fukamachi, Hosoya & Okunuki, 1976a) of the present series, the energy dependence of diffracted intensities was discussed for energy-dispersive diffractometry on GaAs with a solid-state detector (SSD) in the energy range near the As K absorption edge. The observed and calculated results were compared

with each other in both symmetric Laue and symmetric Bragg cases. In Part II (Fukamachi, Hosoya & Okunuki, 1976b), it was confirmed theoretically as well as experimentally that the intensity ratio of a Friedel pair of h and \bar{h} reflexions is given by $|F_h|^2/|F_{\bar{h}}|^2$ both for perfect and mosaic crystals in symmetric Laue and symmetric Bragg cases.

In the present paper, the integrated reflexion power for a perfect GaAs crystal has been measured by the energy-dispersive method with an energy resolution of 1 eV, which is higher than the 5 eV in Parts I and II, in the energy region near the K absorption edges of Ga and As. Then the fine structures in the measured

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curves have been examined. These structures are somewhat similar to those for GaP reported by Fukamachi & Hosoya (1975), and are ascribed to the fine structures of the anomalous scattering factors.

The real part f' has been calculated from the measured values of the imaginary part f'' by the use of the dispersion relation in a better way than that used previously (Fukamachi & Hosoya, 1975). The f'' values outside the range of measurements have been approximated by an empirical formula. With these values of f'' and f' , the curves of integrated reflexion power near the edges have been calculated by the use of formulae shown in Parts I and II. The curves thus obtained agreed reasonably with the measured ones.

Measurements of f'' values

Between the linear absorption coefficient and the imaginary part of the electron polarizability, the relation

$$\mu(\omega) = -\frac{\omega}{c} \varphi_{0i} \quad (1)$$

holds as was indicated in Part I (Fukamachi *et al.*, 1976a). For a GaAs single crystal, φ_{0i} is expressed by

$$\begin{aligned} \varphi_{0i} &= -\frac{c}{\omega} [\mu_{\text{Ga}}(\omega) + \mu_{\text{As}}(\omega)] \\ &= -\frac{16\pi}{V\omega^2} [f''_{\text{Ga}}(\omega) + f''_{\text{As}}(\omega)] \quad (2) \end{aligned}$$

in terms of μ and f'' for Ga and As. Measurements were carried out in the same way as elsewhere (Fukamachi & Hosoya, 1975; Fukamachi, Hosoya, Okunuki & Matsudo, in preparation). In the present work, the contribution from K electrons only to the absorp-

tion coefficients, μ_{Ga} and μ_{As} , is considered. In accordance with this, their measured values have been taken by drawing the zero level on the low-energy side for the respective edge. The 600 reflexion from an MgO monochromator was used for measuring the linear absorption coefficient μ_{Ga} , and the 800 reflexion, for μ_{As} ; the energy resolution was 0.6 and 0.4 eV respectively. The measured values of f''_{Ga} and f''_{As} are shown by solid lines in Fig. 1. The curve at the edge is steeper in f''_{As} than in f''_{Ga} , and fine structures on the high-energy side are somewhat different. Such fine structures cannot be predicted by Hönl's theory (Hönl, 1933a, b), which is not applicable to the range very near the edges.

Calculation of f'

In this section, a brief discussion is given on the method of determining $f'_n(\omega)$ from the observed values $f''_n(\omega)$ by the use of the dispersion relation, before the calculated results are shown. A suffix n denotes each energy level.

The anomalous scattering factors are given by (Fukamachi, Shimamoto, Ohtsuki & Hosoya, 1975)

$$f' = \sum_n f'_n \quad \text{and} \quad f'' = \sum_n f''_n,$$

where

$$\begin{aligned} f'_n(\omega) &= -\frac{1}{2} \int_0^\infty \omega_{in} \left(\frac{dg}{d\omega} \right)_{in} \\ &\times \left(\frac{\omega_{in} - \omega}{(\omega_{in} - \omega)^2 + \Gamma_{in}^2/4} + \frac{\omega_{in} + \omega}{(\omega_{in} + \omega)^2 + \Gamma_{in}^2/4} \right) d\omega_{in}, \quad (3) \end{aligned}$$

and

$$f''_n(\omega) = -\frac{1}{2} \int_0^\infty \omega_{in} \left(\frac{dg}{d\omega} \right)_{in} \frac{\Gamma_{in}/2}{(\omega_{in} - \omega)^2 + \Gamma_{in}^2/4} d\omega_{in}, \quad (4)$$

$dg/d\omega$ is the oscillator density and ω_{in} the transition energy from the ground state n to the excited state i .

In most theoretical papers (*e.g.* Fukamachi & Hosoya, 1975), the value of $(dg/d\omega)_{in}$ has been assumed to change sufficiently slowly in comparison with the Lorentz function, the rest of the integrand, and the term $(dg/d\omega)_{in}$ has been removed from the integral: *i.e.* the approximation $\Gamma_{in} \rightarrow 0$ in the integrand has been adopted. Thus the oscillator density is expressed by

$$\left(\frac{dg}{d\omega} \right)_n \simeq \frac{2}{\pi\omega} f''_n(\omega).$$

However, according to the considerations based on the band calculation (Fukamachi, *et al.*, 1975), the value of $dg/d\omega$ in the energy region near the absorption edge changes more rapidly than the Lorentz function, and the fine structures depend not only upon the state density of the valence electron but also upon the oscillator strength g . Therefore, the value of $f''_n(\omega)$ at present should be defined by (4). In spite of this, the oscillator density is expressed by

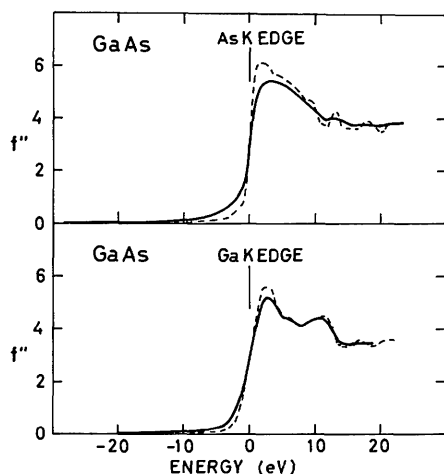


Fig. 1. The f''_K curves as measured are shown near the K absorption edges by solid lines: $E_K = 10.368$ keV for Ga and $E_K = 11.863$ keV for As. Broken lines are those values of f''_K obtained from measured values after the deconvolution with the resolution function. The low-energy side is taken as zero level for each case.

$$\frac{dg}{d\omega} = \frac{2}{\pi\omega} \{f''_n(\omega)\}_{\Gamma_{in} \rightarrow 0} \quad (5)$$

because of convenience in calculation procedures in the present treatment. When (5) is substituted in (4), the following relation is obtained:

$$f''_n(\omega) = \frac{1}{\pi} \int_0^{\infty} \{f''_n(\omega_{in})\}_{\Gamma_{in} \rightarrow 0} \frac{\Gamma_{in}/2}{(\omega_{in} - \omega)^2 + \Gamma_{in}^2/4} d\omega_{in}. \quad (6)$$

If necessary, the value of $\{f''_n(\omega_{in})\}_{\Gamma_{in} \rightarrow 0}$ can be obtained by deconvolution of $f''_n(\omega)$ with the Lorentz function.

In the present calculation, the value of Γ_{in} was approximated to be the classical damping factor at the absorption edge. A comparison between the values of f'' before and after the deconvolution is given in Fig. 1, where $\{f''_n(\omega)\}_{\Gamma_{in} \rightarrow 0}$ is indicated by a broken line. Outside the measured energy range, $\{f''_n(\omega)\}_{\Gamma_{in} \rightarrow 0}$ is assumed to be given by an empirical formula

$$\begin{aligned} \{f''_n(\omega)\}_{\Gamma_{in} \rightarrow 0} &= \frac{\pi}{2} \left(\frac{\omega_n}{\omega}\right)^{q_n-1} (q_n-1)g_n & \omega > \omega_n \\ &= 0 & \omega < \omega_n, \end{aligned} \quad (7)$$

where g_n is the oscillator strength at energy ω_n , the relevant absorption edge. In this calculation, the values of q_n and g_n are those of Cromer (1965). In this way, $\{f''_n(\omega)\}_{\Gamma_{in} \rightarrow 0}$ is given in the whole range of ω .

In order to obtain $f'_n(\omega)$ values by numerical integration, the following relation was used:

$$\begin{aligned} f'_n(\omega) &= -\frac{1}{\pi} \int_0^{\infty} \{f''_n(\omega_{in})\}_{\Gamma_{in} \rightarrow 0} \\ &\times \left(\frac{\omega_{in} - \omega}{(\omega_{in} - \omega)^2 + \Gamma_{in}^2/4} + \frac{\omega_{in} + \omega}{(\omega_{in} + \omega)^2 + \Gamma_{in}^2/4} \right) d\omega_{in}. \end{aligned} \quad (8)$$

Therefore, the precision of the approximation of (7) affects that of the absolute values of f'_n through calculation especially near the absorption edge. The $f'_n(\omega)$ and $f''_n(\omega)$ curves of GaAs thus obtained are shown in Figs. 2 and 3, where Hönl's values are also shown by broken lines for comparison. The contribution of the L electrons was taken into account by the use of the empirical formula (7), while no correction has been made for the M electrons.

Measurements for integrated reflexion power near the K absorption edges

A detailed discussion on the method of obtaining the integrated reflexion power has been already given in Part I for an energy-dispersive diffractometer with an SSD and continuous X-rays. The following points are to be noted in the present experiment: the specimen used is same as that used in the previous measurements (Parts I & II) but the energy resolution has been im-

proved to the value of 0.9 eV for the Ga K absorption edge and 1.5 eV for the As K edge.

Integrated intensities in the symmetric Bragg case were measured for 555 and $\bar{5}\bar{5}\bar{5}$ reflexions near the

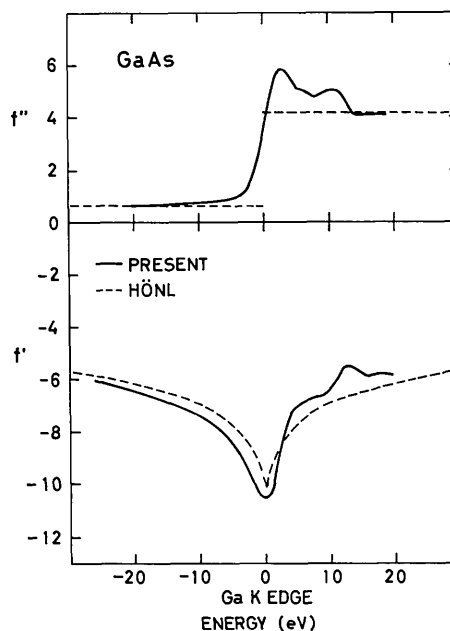


Fig. 2. Anomalous scattering factors f' and f'' near the Ga K edge are compared with those obtained by Hönl's theory. In the upper, the solid line is measured values of f'' as shown in Fig. 1, while in the lower, the solid line is the present values of f'' obtained by the dispersion relation. The broken lines in both figures are those from Hönl's theory.

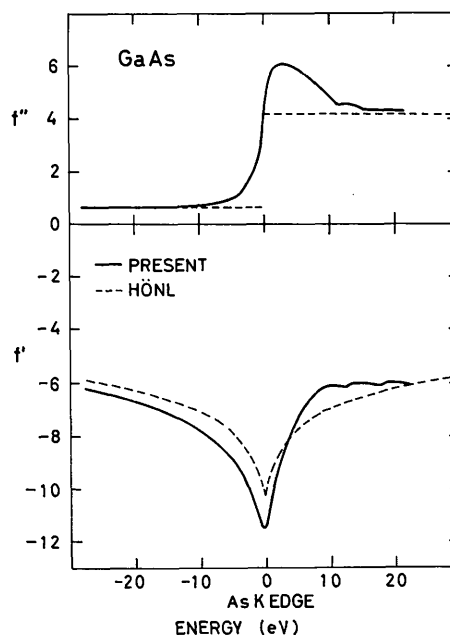


Fig. 3. Anomalous scattering factors near the As K edge. The lines are similar to those in Fig. 2.

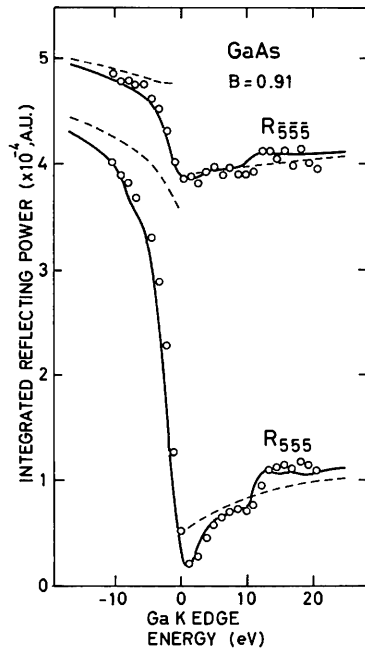


Fig. 4. Integrated reflecting powers of the 555 Friedel pair from GaAs near the Ga K absorption edge in the Bragg case. Measured values are indicated by the open circles. The solid lines were calculated with the anomalous scattering factors determined by the present method, and the broken lines were obtained by Hönl's theory. The measured values of R_{555} were scaled to calculated values on the higher energy side.

K absorption edges. The coordinates of atoms are taken as described in Part I, p. 107. The results are given in Figs. 4 and 5, where the fine structures are clearly seen mainly above the absorption edges. Above the Ga K edge (Fig. 4), R_{555} has two stages of intensity changes and the relation $R_{555} > R_{555}$ holds in the whole measured range. On the other hand, in the region near the As K edge (Fig. 5), R_{555} shows a sharp intensity change very near the edge, while R_{555} only a slight change. The intensities of this Friedel pair are reversed in magnitude as shown in Fig. 5. However, the point where two R values are equal does not exactly fall on the edge.

Calculation of integrated reflecting power

By the use of the anomalous scattering factors obtained in the above, the integrated reflecting power in the symmetric Bragg case can be calculated, as was given by equation (12) of Part II, expressed by

$$R_h = \frac{\omega_B C |\varphi_{hr}|_B}{2 \sin^2 \theta_B} \frac{1 + |k|^2 - 2|k| \sin \delta}{\{(1 - |k|^2)^2 + 4|k|^2 \cos^2 \delta\}^{1/2}} \times \int_{W_{\min}}^{W_{\max}} [\mathcal{L}(W) + \{\mathcal{L}^2(W) - 1\}^{1/2}]^{-1} dW, \quad (9)$$

where

$$\mathcal{L}(W) = \frac{\sqrt{[W^2 - 1 - g_B^2 + |k|^2]^2 + 4(g_B W - |k| \cos \delta)^2} + W^2 + g_B^2}{\{(1 - |k|^2)^2 + 4|k|^2 \cos^2 \delta\}^{1/2}}, \quad (10)$$

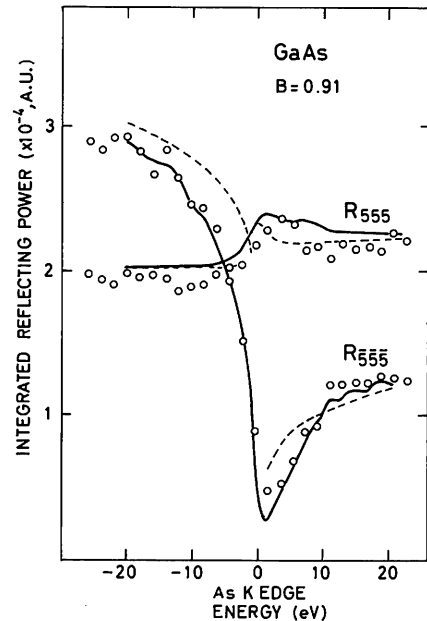


Fig. 5. Integrated reflecting powers of the 555 Friedel pair near the As K edge. Other features are similar to those of Fig. 4.

as was given by (25) of Part I, and W_{\max} and W_{\min} are assumed to be ΔW and $-\Delta W$, respectively, which are determined by the energy resolution $\Delta\omega$ of the slit system. The integration in (9) was numerically carried out. It should be noted that $|\varphi_{hr}|_B$ and $g_B = \varphi_{0i}/|\varphi_{hr}|_B$ depend on temperature through the Debye parameter B . The average value of B 's for Ga and As atoms was determined to be 0.91 \AA^2 by a powder intensity measurement (Uno, Okano & Yukino, 1970). This B value has been used in the present calculation, although it was entirely neglected in Parts I and II.

Comparison between measurements and calculations

The f'' values were obtained from the measurements of the absorption coefficient in the energy regions near the K absorption edges of GaAs, and then f' values were calculated by the use of the dispersion relation. With these values, the values of integrated reflecting power were calculated as described in the previous section, and compared with the measured results and with the calculated results by Hönl's method in Figs. 4 and 5 for the Ga and As K absorption edges respectively.

In the present integrated reflecting power measured near the K absorption edges, the energy resolution is better than those reported in Parts I and II (Fukamachi *et al.*, 1976a, b). The solid curves for R values include experimental information through f'' values, and show much better correspondence to the measured values than the curves calculated by Hönl's anomalous scattering factor; the present calculations of integrated

reflecting powers reproduce the continuous and steep intensity rise below the K edges and more or less the fine structures on the high-energy side.

Merits in applications

The phase determination may generally be facilitated by the possible use of any energy from the white radiation, since bigger changes can be expected for intensities because of anomalous scattering factors very near the absorption edge (Hosoya, 1975). The application in this field will become easier and more popular particularly when intense X-rays from an electron synchrotron or a storage ring are available. In such cases, the incident X-rays with desired energy may usually be chosen by a monochromator different from the present.

In order to utilize the anomalous scattering in a certain energy range, it is necessary to know anomalous scattering factors for any crystal of unknown structure, whether it is polar or not. For this purpose, the present method is very useful, because it is possible to determine $f'(\omega)$ without knowing the structure by the measurement of the absorption coefficient, if only a sample crystal is available as a thin plate with the necessary minimum area. As shown in the measurement of extended X-ray absorption fine structure (EXAFS) by Kincaid & Eisenberger (1975) with radiation from a storage ring, it does not take much time to measure the absorption coefficient, which also makes the present method useful. When more than one anomalous scatterer with a different environment is present in a unit cell, the energy dependences of f'' and, therefore, of f' show their average values. This makes the applications less effective but perhaps not very much.

There are a few kinds of more direct methods of measuring the f' values with an X-ray interferometer (Bonse & Hellkötter, 1969; Creagh & Hart, 1970; Bonse & Materlik, 1972; Cusatis & Hart, 1975; Bonse & Materlik, 1975*a, b*). In these methods also, it is not necessary to know the structure. However, these methods, though elegant and accurate, seem to be more elaborate and need specimens of greater area. Besides, in energy-dispersive diffractometry, it is anyway necessary for structure analyses to measure the absorption coefficient for the absorption correction in a certain energy range. The present method is useful for this too.

Discussion

In order to improve the precision of the present calculated $f'(\omega)$ values, the following two corrections should be taken into account. One is the effect of inelastic scattering, such as thermal diffuse and Compton scattering, on the linear absorption coefficient $\mu(\omega)$. This effect causes errors in $f'(\omega)$ through $f''(\omega)$, because the dispersion relation has been used. The other is the use of $f'(\omega)$ values approximated by an em-

pirical formula outside the range of measurements, although this problem does not seem to be so serious within the present results. On the other hand, minor disagreement of integrated reflexion powers between theory and experiment can be attributed at least partly to the effect of thermal vibration rather than to the lack of precision in anomalous scattering factors.

Fukamachi & Hosoya (1975) have proposed a method of determining $f'(\omega)$ through the intensity ratio between Friedel pair reflexions h and \bar{h} . This method enables us to obtain the anomalous scattering factors only for a polar crystal, but cannot be applied to either non-polar crystals or crystals with unknown structures. In Part IV of the present series, the obtained values of $f'(\omega)$ will be compared with the experimental results obtained by the intensity ratio of a Friedel pair described in the above. Such a comparison has already been made for GaP (Fukamachi & Hosoya, 1975), but the energy resolution was worse than in the present work. However, this is a more direct way of discussing the precision of the $f'(\omega)$ values calculated by the present method.

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