

On Different Probabilistic Approaches to Quartet Theory*

BY C. GIACOVAZZO

Istituto di Mineralogia e Petrografia dell'Università, 70121 Bari, Italy

(Received 1 June 1976; accepted 2 July 1976)

The new probabilistic approach applied by Hauptman to quartet invariants is compared with the method used by Giacovazzo. It is shown that the two approaches can lead to mathematically identical distributions even if they start with conceptually different postulates: the reciprocal vectors are the primitive random variables in the first approach, the positional parameters in the second. The probabilistic meanings of some conclusive phase relationships are discussed.

Introduction

Phase relations between four linearly dependent reflexions \mathbf{h} , \mathbf{k} , \mathbf{l} , $\mathbf{h} + \mathbf{k} + \mathbf{l}$ have been shown to be useful for the direct solution of crystal structures. Schenk (1973) discussed such quartets and gave an estimate of the quartet cosine invariant by constructing each quartet from the difference of the phases of two triplets relative to the same reflexion.

More reliable estimates of the quartet cosine invariant have recently been given, *via* the method of the joint probability distribution functions, by Hauptman (1975*a,b*), Green & Hauptman (1976), Hauptman & Green (1976) and Giacovazzo (1975, 1976*a,b,c*).

Giacovazzo's probabilistic approach generalizes the original Klug (1958) formalism, which develops the joint distribution functions in a strictly asymptotic series in powers of $N^{-1/2}$, where N is the number of equal atoms in the cell. From a statistical point of view the crystallographic problem is clear: the joint distribution

$$P(E_1, E_2, \dots, E_n)$$

involves a number of structure factors each of which is a linear sum of random variables (the atomic contributions to the structure factors). In X-ray diffraction experiments the reciprocal vectors are known parameters, while the atomic coordinates are not. So it may be convenient to consider in the statistical interpretation of the phase problem the atomic positions as random variables.

A different basis was postulated in the probabilistic approach introduced by Hauptman (1975*a,b*) and used also by Hauptman & Green (1976): the crystal structure is assumed to be fixed as well as one or more reciprocal vectors, while one or more other vectors are assumed to be the random variables.

It is evident that the distribution based on atomic coordinates as the independent variables is conceptually distinct from that in which it is assumed that the reciprocal vectors are random variables. Nevertheless both types of distribution require that the fractional

part of \mathbf{hr} is uniformly distributed in the interval (0,1). A question arises: Owing to the symmetrical role played by \mathbf{h} and \mathbf{r} in the two kinds of distribution, can one expect mathematically equivalent results from distributions conceptually distinct? Green & Hauptman (1976) have claimed that there is no reason to suppose that the two kinds of distribution can lead to identical results. Their conclusion was: 'Again, it should be stressed that it is our distribution which is the appropriate one for crystal structure analysis, ..., since one is ordinarily given a fixed but unknown crystal structure, and structure factor amplitudes are sampled from reciprocal space'. The final phase relationships, obtained by application of the two kinds of distribution to the quartet cosine invariants, seem to justify Hauptman & Green's conclusions. In fact Giacovazzo's approach led to the statement that a quartet cosine

$$\cos(\varphi_{\mathbf{h}} + \varphi_{\mathbf{k}} + \varphi_{\mathbf{l}} - \varphi_{\mathbf{h}+\mathbf{k}+\mathbf{l}})$$

is probably positive when

$$|E_{\mathbf{h}+\mathbf{k}}|^2 + |E_{\mathbf{h}+\mathbf{l}}|^2 + |E_{\mathbf{k}+\mathbf{l}}|^2 > 2.$$

On the contrary, from the Hauptman approach, the sign of a quartet cosine depends on an intricate inter-relationship among all the seven magnitudes

$$|E_{\mathbf{h}}|, |E_{\mathbf{k}}|, |E_{\mathbf{l}}|, |E_{\mathbf{h}+\mathbf{k}+\mathbf{l}}|, |E_{\mathbf{h}+\mathbf{k}}|, |E_{\mathbf{h}+\mathbf{l}}|, |E_{\mathbf{k}+\mathbf{l}}|.$$

In the present paper we will show that the two distributions are mathematically equivalent when applied to quartet invariants; furthermore, they are in principle equally appropriate for crystal structure analysis. In particular Giacovazzo's approach will prove able to obtain Hauptman's distributions and *vice versa*. The algebraic differences between the final phase relationships described in the quoted papers are shown to be essentially due to the different physical meanings of the formulae and not to the kinds of distribution. This study will enable us to generalize the phase relationships obtained in the quoted papers.

A general expression for the characteristic function

For a structure consisting of N identical point atoms in a non-centrosymmetric space group of order m a general normalized structure factor $E_{\mathbf{h}}$ is defined by

* *Editorial Note.* A few days after this paper was received, a paper containing essentially the same results was submitted by J. J. L. Heinerman, Laboratorium voor Structuurchemie, Rijksuniversiteit, Padualaan 8, Utrecht, The Netherlands. The editors greatly regret that space does not permit the publication of both papers.

$$E_{\mathbf{h}} = A_{\mathbf{h}} + iB_{\mathbf{h}} = N^{-1/2} \sum_{j=1}^t \zeta(\mathbf{h}) \\ = N^{-1/2} \sum_{j=1}^t \zeta_j(\mathbf{h}) + i\eta_j(\mathbf{h}),$$

where ζ and η are the trigonometric functions for the real and imaginary parts of the structure factor, t is the number of independent atoms in the unit cell. The joint probability function

$$P(A_{\mathbf{h}_1}, A_{\mathbf{h}_2}, \dots, A_{\mathbf{h}_n}; B_{\mathbf{h}_1}, B_{\mathbf{h}_2}, \dots, B_{\mathbf{h}_n})$$

is found by taking the Fourier transform of the characteristic function

$$C(u_1, u_2, \dots, u_n; v_1, v_2, \dots, v_n),$$

where $u_j, v_j, j=1, \dots, n$, are carrying variables associated respectively with $A_{\mathbf{h}_j}$ and $B_{\mathbf{h}_j}$ values.

It is possible to find an algebraic expression for C which does not formally depend on the choice of the primitive random variables. In accordance with Klug (1958) and Karle & Hauptman (1958)

$$C(u_1, \dots, u_n; v_1, \dots, v_n) \\ = \langle \exp i(u_1 A_1 + u_2 A_2 + \dots + v_n B_n) \rangle \\ = \left\langle \exp \left\{ iN^{-1/2} \left[u_1 \sum_{j=1}^t \zeta_j(\mathbf{h}_1) \right. \right. \right. \\ \left. \left. \left. + u_2 \sum_{j=1}^t \zeta_j(\mathbf{h}_2) + \dots + v_n \sum_{j=1}^t \eta_j(\mathbf{h}_n) \right] \right\} \right\rangle \\ = \prod_{j=1}^t \langle \exp iN^{-1/2} [u_1 \zeta_j(\mathbf{h}_1) \\ + u_2 \zeta_j(\mathbf{h}_2) + \dots + v_n \eta_j(\mathbf{h}_n)] \rangle \\ = \prod_{j=1}^t {}^j C(N^{-1/2} u_1, N^{-1} u_2, \dots, N^{-1/2} v_n). \quad (1)$$

${}^j C$ is the characteristic function of the joint probability distribution of the contributions of the j th atom to the structure factors $E_{\mathbf{h}_1}, \dots, E_{\mathbf{h}_n}$. Equation (1) is the required expression for C . According to whether the \mathbf{h} reciprocal vectors or the \mathbf{r} vectors are the primitive random variables, the average in (1) must be taken over \mathbf{h} or over \mathbf{r} . By the changes of variable

$$u_j = \varrho_j \cos \psi_j, \quad v_j = \varrho_j \sin \psi_j \\ A_j = R_j \cos \varphi_j, \quad B_j = R_j \sin \varphi_j,$$

(1) becomes in $P1$

$$C(\varrho_1, \dots, \varrho_n; \psi_1, \dots, \psi_n) \\ = \langle \exp i[\varrho_1 R_1 \cos(\psi_1 - \varphi_1) + \dots \\ + \varrho_n R_n \cos(\psi_n - \varphi_n)] \rangle \\ = \prod_{j=1}^n \langle \exp iN^{-1/2} [\varrho_1 \cos(2\pi \mathbf{h}_1 \mathbf{r}_j - \psi_1) + \dots \\ + \varrho_n \cos(2\pi \mathbf{h}_n \mathbf{r}_j - \psi_n)] \rangle. \quad (2)$$

Equation (2.4) of Hauptman (1975a) and our approach are both in accordance with (2).

The mathematical approaches

Different approaches have been used by Hauptman and Giacobozzo in order to derive the explicit expression of (1). Giacobozzo (1975, 1976a) introduced for each ${}^j C$ the multivariate cumulant generating function

$${}^j K(iu_1, \dots, \dots, iv_n) = \log {}^j C(u_1, \dots, \dots, v_n),$$

which expanded in the series of cumulants, gives

$$C(u_1, \dots, \dots, v_n) = \exp \left[\sum_{j=1}^t \sum_{r+s+\dots+w=2}^{\infty} N^{-(r+s+\dots+w)/2} \right. \\ \left. \times \frac{{}^j K_{rs\dots w}}{r!s!\dots w!} (iu_1)^r (iu_2)^s \dots (iv_n)^w \right]. \quad (3)$$

${}^j K_{rs\dots w}$ is the cumulant of order $r+s+\dots+w$ of the generating function ${}^j K$. If the standardized cumulants ${}^j \lambda_{rs\dots w}$ are introduced (they are marked by the property $\lambda_{200\dots} = \lambda_{020\dots} = \dots = 1$), (3) becomes

$$C(u_1, \dots, \dots, v_n) = \exp \left[\sum_{j=1}^t \sum_{r+s+\dots+w=2}^{\infty} 2^{-(r+s+\dots+w)/2} \right. \\ \left. \times \frac{{}^j \lambda_{rs\dots w}}{r!s!\dots w!} \left(\frac{iu_1}{t^{1/2}} \right)^r \left(\frac{iu_2}{t^{1/2}} \right)^s \dots \left(\frac{iv_n}{t^{1/2}} \right)^w \right] \\ = \exp \left[\sum_{v=2}^{\infty} \frac{S_v}{t^{v/2}} \right], \quad (4)$$

where

$$S_v = \sum_{r+s+\dots+w=v} \sum_{j=1}^t (2)^{-v/2} \\ \times \frac{{}^j \lambda_{rs\dots w}}{r!s!\dots w!} (iu_1)^r (iu_2)^s \dots (iv_n)^w. \quad (5)$$

The Taylor's series of (4) was used in Giacobozzo's approach. Hauptman's formalism seems superior. In fact it is able to derive an accurate expression for ${}^j C$ [g_{λ} in Hauptman's (1975a) notation; see equation (II.29)] but suffers from two approximations (see Appendices I and III, Hauptman, 1975a). The first is the Taylor expansion of the Bessel function $J_m(z)$:

$$J_m(z) = \frac{z^m}{2^m \Gamma(m+1)} \left\{ 1 - \frac{z^2}{4(m+1)} + \dots \right\}.$$

The second is the Taylor expansion of the logarithmic function

$$\log {}^j C = {}^j C - 1 + \dots$$

In conclusion, the algebraic expression of the characteristic function obtained by Hauptman (1975a; equation III.3) coincides with (4). As the joint distribution function is unequivocally fixed by the characteristic function, the same phase relationships are obtainable whether the reciprocal vectors are the primitive random variables or not.

From a general point of view both postulates, *i.e.* the reciprocal vectors are the primitive random variables as long as the structure is fixed and *vice versa*,

seem to us to be equally appropriate for crystal structure analysis. Their distributions may give, according to circumstances, equal or complementary results and deserve to be simultaneously pursued.

Some considerations about quartet phase relationships

In accordance with Hauptman, let us make use of the characteristic function of the exponential form (4). For the sake of simplicity we refer to $P\bar{I}$. If we introduce the concept of joint probability distribution of signs of structure factors (Naya, Nitta & Oda, 1964)

$$P(S_1, \dots, S_n) = \frac{P(R_1 S_1, \dots, R_n S_n)}{\sum_{S_1=\pm 1} \dots \sum_{S_n=\pm 1} P(R_1 S_1, \dots, R_n S_n)},$$

we obtain for the sign of a quartet, the relationship

$$P_+ = \frac{e^{-B} \cdot F^+}{e^{-B} \cdot F^+ + e^B \cdot F^-},$$

where $B = 2R_1 R_2 R_3 R_4 / N$,

$$F^\pm = \cosh \left[Z_{12}^\pm \left(\frac{R_{12}}{\sqrt{N}} - \frac{R_{23} R_{31}}{N} \right) \right] \\ \times \cosh \left[Z_{23}^\pm \left(\frac{R_{23}}{\sqrt{N}} - \frac{R_{12} R_{31}}{N} \right) \right]$$

$$\times \cosh \left[Z_{31}^\pm \left(\frac{R_{31}}{\sqrt{N}} - \frac{R_{12} R_{23}}{N} \right) \right] \\ + \cosh \left[Z_{12}^\pm \left(\frac{R_{12}}{\sqrt{N}} + \frac{R_{23} R_{31}}{N} \right) \right] \\ \times \cosh \left[Z_{23}^\pm \left(\frac{R_{23}}{\sqrt{N}} + \frac{R_{12} R_{31}}{N} \right) \right] \\ \times \cosh \left[Z_{31}^\pm \left(\frac{R_{31}}{\sqrt{N}} + \frac{R_{12} R_{23}}{N} \right) \right] \\ + \sinh \left[Z_{12}^\pm \left(\frac{R_{12}}{\sqrt{N}} - \frac{R_{23} R_{31}}{N} \right) \right] \\ \times \sinh \left[Z_{23}^\pm \left(\frac{R_{23}}{\sqrt{N}} - \frac{R_{12} R_{31}}{N} \right) \right] \\ \times \sinh \left[Z_{31}^\pm \left(\frac{R_{31}}{\sqrt{N}} - \frac{R_{12} R_{23}}{N} \right) \right] \\ - \sinh \left[Z_{12}^\pm \left(\frac{R_{12}}{\sqrt{N}} + \frac{R_{23} R_{31}}{N} \right) \right] \\ \times \sinh \left[Z_{23}^\pm \left(\frac{R_{23}}{\sqrt{N}} + \frac{R_{12} R_{31}}{N} \right) \right] \\ \times \sinh \left[Z_{31}^\pm \left(\frac{R_{31}}{\sqrt{N}} + \frac{R_{12} R_{23}}{N} \right) \right]. \quad (6)$$

Table 1. Number of relations (nr) and percentage of correct negative quartet relations for a 40-atom model structure

Tanh (arg)	Two cross-vectors in measurements				Three cross-vectors in measurements			
	Our approach		Hauptman's approach		Our approach		Hauptman's approach	
	nr	%	nr	%	nr	%	nr	%
0.4	76	89.5	148	89.2	340	95.3	1136	88.4
0.6	8	100	12	100	76	100	280	97.1
0.8					20	100	80	100
1.0							8	100

Table 2. Number of relations (nr) and percentage of correct positive quartet relations for a 40-atom model structure

Tanh (arg)	Two cross-vectors in measurements				Three cross-vectors in measurements			
	Our approach		Hauptman's approach		Our approach		Hauptman's approach	
	nr	%	nr	%	nr	%	nr	%
0.4	4623	98.3	10843	93.4	4640	98.0	7872	94.7
0.6	2616	99.2	6976	96.6	2812	98.7	5644	97.6
0.8	1613	99.8	4501	98.2	1760	99.3	3928	99.1
1.0	1054	100	2957	99.1	1116	100	2632	99.5
1.2	738	100	2010	99.8	764	100	1720	99.6
1.4	519	100	1354	99.7	516	100	1124	100
1.6	363	100	899	100	368	100	728	100
1.8	267	100	591	100	288	100	496	100
2.1	179	100	327	100	184	100	260	100
2.4	140	100	195	100	148	100	156	100
2.7	100	100	124	100	124	100	84	100
3.0	64	100	96	100	76	100	56	100
3.5	24	100	24	100	60	100	40	100
4.0	24	100	4	100	44	100	4	100
5.0	4	100			12	100	4	100
6.0					4	100		
7.0					4	100		
8.0					4	100		
9.0					4	100		
10.0					4	100		

In accordance with Hauptman's notation, the E_j 's are the base vectors of the quartet, the E_{ij} 's are the cross vectors, and

$$\begin{aligned} Z_{12}^{\pm} &= R_1 R_2 \pm R_3 R_4, \\ Z_{23}^{\pm} &= R_2 R_3 \pm R_1 R_4, \\ Z_{31}^{\pm} &= R_3 R_1 \pm R_2 R_4. \end{aligned}$$

Equation (6) reduces to (3.13) of Hauptman & Green (1976) when the products $R_{ij}R_{jk}/N$ are negligible in comparison with R_{ik}/\sqrt{N} (which occurs in most structures). Let us now derive from the Hauptman distribution the value

$$\langle V \rangle = \langle E_{h_1} E_{h_2} E_{h_3} E_{h_1+h_2+h_3} \rangle.$$

One obtains

$$\langle V \rangle \simeq \frac{1}{Q} \cdot \frac{1}{N} (R_{12}^2 + R_{31}^2 + R_{23}^2 - 2),$$

which is a value already given by Giacovazzo (1975, equation 10). If the value of $\langle V^2 \rangle$ is also calculated, the probability distribution of the random variable V may be expanded in a Gram-Charlier series which, stopped to the first terms, gives a normal distribution for V . Hauptman's distribution gives then a conclusive relationship equivalent to

$$P^+ \simeq 0.5 + 0.5$$

$$\times \tanh \left\{ \frac{1}{N} R_1 R_2 R_3 R_4 \frac{(R_{12}^2 + R_{31}^2 + R_{23}^2 - 2)}{1 + 4[R_{12}^2 + R_{13}^2 + R_{23}^2 - 3]/N} \right\}, \quad (7)$$

already derived by Giacovazzo (1975, equation 13). We wish to emphasize that (6) and (7) have different physical meanings. (6) makes use of the concept of the sign distribution of the structure factors; the value of P^+ , in fact, is calculated given the seven magnitudes R_h, R_k, \dots, R_{k+1} . On the contrary (7) postulates that a quartet has the same sign as its expected value

$$\begin{aligned} \langle V \rangle &= \int_{-\infty}^{+\infty} \dots \int_{-\infty}^{+\infty} E_h E_k E_l E_{h+k+1} \\ &\times P(E_h, \dots | R_{h+k}, R_{h+l}, R_{k+1}) dE_h \dots dE_{h+k+1}. \end{aligned}$$

The estimation of $\langle V \rangle$ requires a fourfold integration on the basis vectors from $-\infty$ to $+\infty$, and not merely on the signs as in (6). It comes therefore as no surprise that the positivity of a quartet depends, according to Giacovazzo, on the magnitudes of the cross vectors; according to Hauptman, on an intricate interrelationship among all seven magnitudes.

Experimental

A comparison between the general reliabilities of the sign relationships obtained by Hauptman & Green and by Giacovazzo is made in Tables 1-4. In order to make clear the comparison, we note:

Table 3. Total number of relations and percentage of correct relations for a 40-atom model structure

Tanh (arg)	Our approach		Hauptman's approach	
	nr	%	nr	%
0.4	9679	98.0	19999	93.6
0.6	5512	99.0	12903	97.0
0.8	3393	99.5	8509	98.6
1.0	2170	100	5597	99.3
1.2	1502	100	3730	99.7
1.4	1035	100	2478	99.7
1.6	731	100	1627	100
1.8	555	100	1087	100
2.1	363	100	587	100
2.4	288	100	351	100
2.7	224	100	208	100
3.0	140	100	152	100
3.5	84	100	64	100
4.0	68	100	8	100
5.0	16	100	4	100
6.0	4	100		
7.0	4	100		
8.0	4	100		
9.0	4	100		
10.0	4	100		

Table 4. Total number of relations and percentage of correct relations for a 100-atom model structure

Tanh (arg)	Our approach		Hauptman's approach	
	nr	%	nr	%
0.4	2812	96.3	11204	86.6
0.6	1192	99.0	5588	92.8
0.8	504	100	2988	96.0
1.0	292	100	1668	96.9
1.2	120	100	820	99.5
1.4	44	100	480	100
1.6	24	100	252	100
1.8	20	100	160	100
2.1	8	100	56	100
2.4	4	100	16	100
2.7			8	100
3.0			4	100

- (a) the formulae are tested in $P\bar{1}$ for two model structures with $N=40$ and $N=100$.
- (b) Quartets in which two and three cross vectors are contained in the measurements are both checked in the tables. The formulae under test are those given by Giacovazzo (1976b, equations 11, 12) and by Hauptman & Green (1976, equation 3.13). Even if the Hauptman approach is quite general, formulae for quartets in which only two cross vectors are in the measurements were not explicitly derived by Hauptman & Green. For them we have obtained (Giacovazzo, 1976d) when R_{12} is the absent reflexion,

$$P_{\pm} \simeq \frac{1}{L} \exp(\mp B/2) \cosh \frac{R_{23} Z_{23}^{\pm}}{\sqrt{N}} \cosh \frac{R_{31} Z_{31}^{\pm}}{\sqrt{N}},$$

where

$$\begin{aligned} L = & \exp(-B/2) \cosh \frac{R_{23} Z_{23}^{+}}{\sqrt{N}} \cosh \frac{R_{31} Z_{31}^{+}}{\sqrt{N}} \\ & + \exp(+B/2) \cosh \frac{R_{23} Z_{23}^{-}}{\sqrt{N}} \cosh \frac{R_{31} Z_{31}^{-}}{\sqrt{N}}. \end{aligned}$$

- (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.

References

- GIACOVAZZO, C. (1975). *Acta Cryst.* A **31**, 252–259.
 GIACOVAZZO, C. (1976a). *Acta Cryst.* A **32**, 91–99.
 GIACOVAZZO, C. (1976b). *Acta Cryst.* A **32**, 74–82.
 GIACOVAZZO, C. (1976c). *Acta Cryst.* A **32**, 100–104.
 GIACOVAZZO, C. (1976d). *Acta Cryst.* A **32**, 958–966.
 GREEN, E. A. & HAUPTMAN, H. (1976). *Acta Cryst.* A **32**, 43–45.
 HAUPTMAN, H. (1975a). *Acta Cryst.* A **31**, 671–679.
 HAUPTMAN, H. (1975b). *Acta Cryst.* A **31**, 680–687.
 HAUPTMAN, H. & GREEN, E. A. (1976). *Acta Cryst.* A **32**, 45–49.
 KARLE, J. & HAUPTMAN, H. (1958). *Acta Cryst.* **11**, 264–269.
 KLUG, A. (1958). *Acta Cryst.* **11**, 515–543.
 NAYA, S., NITTA, I. & ODA, T. (1965). *Acta Cryst.* **19**, 734–747.
 SCHENK, H. (1973). *Acta Cryst.* A **29**, 77–82.

Acta Cryst. (1977). A **33**, 54–58

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

BY T. FUKAMACHI,* S. HOSOYA, T. KAWAMURA† AND M. OKUNUKI‡

Institute for Solid-State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo, Japan

(Received 24 May 1976; accepted 7 June 1976)

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

* Present address: Saitama Institute of Technology.

† Permanent address: Department of Applied Physics, Waseda University.

‡ Permanent address: JEOL Ltd.