The white X-ray diffraction method with the use of a powder sample [Laine, Lähteenmäki & Kantola (1972). X-ray Spectrosc. 1, 93–98] was improved by paying special attention to the following four points: (i) the determination of the energy spectrum of incident white X-rays, (ii) the measurement of the energy dependence of the relative absorption coefficient, (iii) the correction for the contribution from thermal diffuse scattering, and (iv) the correction for the anomalous dispersion. The determination of the structure factors of GaP is shown as an example of its applications. The structure factors determined were compared with those obtained by the usual angle dispersive method with monochromatized X-rays on the same sample. It is shown that these two sets of structure factors mostly agree within the limit of reproducibility.

Introduction

The recent improvement of the energy resolution of the solid-state detector (SSD) makes it possible to use it for the measurement of the diffraction pattern of a powder sample in energy space. The pioneer work in this field was done by Giesen & Gordon (1968) for a measurement of the lattice spacings and by Laine, Lähteenmäki & Kantola (1972) for a measurement of the structure factors. The present work is an improvement of the work of Laine et al. (1972).

The energy spectrum of the incident white X-rays was estimated from the integrated intensity of the 220 reflexion of a GaP powder sample at various energies. The energy spectrum thus obtained was modified by the energy dependence of the quantum efficiency of the SSD. However, the relative structure factor free from the influence of the quantum efficiency could be obtained, because the measured integrated intensity was also modified by the same quantum efficiency. Therefore, structure factors of GaP could be determined relative to \( F(220) \).

In order to check the accuracy of the structure factors thus obtained, they were compared with those obtained by the usual angle dispersive method with monochromatized X-rays on the same sample. These two sets of the structure factors mostly showed reasonable agreement.

The method of white X-ray diffraction from a powder sample

For a flat powder sample, the relative integrated intensity of a beam diffracted from the plane \((hkl)\) in the case of symmetric reflexion, \( I_r(hkl) \), is given by (Cole, 1970)

\[
I_r(hkl) = \left[ I_w(E_{hkl}) \mu(E_{hkl}) F_r(hkl)^2 / \mu(E_{hkl}) E_{hkl}^2 \right] \times \left[ (1 + \cos^2 2\theta) / \sin^3 \theta \right],
\]

where \( E_{hkl} \) is the X-ray energy of the reflexion, \( I_w(E_{hkl}) \) the relative intensity of the incident beam, \( \mu(E_{hkl}) \) the relative absorption coefficient, \( F_r(hkl) \) the relative structure factor, \( m(hkl) \) the multiplicity factor and \( \theta \) the Bragg angle. In this equation, \( I_r(hkl) \) and \( E_{hkl} \) can be measured directly from the observed diffraction pattern. The absorption coefficient \( \mu(E_{hkl}) \) can be obtained as follows: if integrated intensity, \( I_{absr}(hkl) \), is measured by putting a thin slice of the sample material in front of the receiving slit, \( \mu(E_{hkl}) \) is given by

\[
\mu(E_{hkl}) = \ln \left[ I_r(hkl) / I_{absr}(hkl) \right].
\]

The intensity \( I_w(E) \) in equation (1) can be obtained by the measurement of the integrated intensity of a standard reflexion of a certain sample at several X-ray energies. This enables us also to determine structure factors relative to that of the standard reflexion. In the present experiment the \( F(220) \) of GaP was used as the standard, because the structure factors of GaP were also obtained by the usual angle-dispersive method.

The contribution of the thermal diffuse scattering to \( F_r(hkl) \) can be corrected by the method shown in a previous paper (Uno & Ishigaki, 1975), if the elastic constants of the sample are known.

The calculated structure factor including anomalous dispersion, \( F_{cal}(hkl) \), is given by

\[
F_{cal}(hkl) = \sum_j \left[ f^0_j(hkl) + A f_j'(E) + i A f_j''(E) \right] \times \exp \left( -B_j \sin^2 \theta / \lambda^2 \right)
= F_{cal}^0(hkl) + A F_{d}(hkl),
\]

where \( f^0_j(hkl) \) is an atomic scattering factor, \( A f_j'(E) \) and \( A f_j''(E) \) are the anomalous-dispersion correction terms, \( B_j \) is the temperature factor, \( F_{cal}^0(hkl) \) the structure factor without anomalous dispersion included and \( A F_{d}(hkl) \) the correction term for anomalous dispersion. The anomalous-dispersion correction terms were calculated after the evaluation by Cromer (1965). The
experimental structure factor corrected for the anomalous dispersion, \( F_{\text{exp}}^{0}(hk\ell) \), is assumed to be given by
\[
F_{\text{exp}}^{0}(hk\ell) = SF_{\text{rc}}(hk\ell) - AF(hk\ell),
\]
where \( S \) is the scale factor, \( F_{\text{rc}}(hk\ell) \) the relative structure factor corrected for the contribution of the thermal diffuse scattering. The parameters, \( S \) and \( B_{j} \), were determined so that the following quantity is minimized:
\[
\langle \Delta q(r)^{2} \rangle = \left( \frac{1}{v} \right) \sum \sum [F_{\text{exp}}^{0}(hk\ell) - F_{\text{cal}}^{0}(hk\ell)]^{2}
\]
\[
= \left( \frac{1}{v} \right) \sum \sum m(hk\ell) [SF_{\text{rc}}(hk\ell) - F_{\text{cal}}(hk\ell)]^{2}.
\]
Then \( F_{\text{exp}}^{0}(hk\ell) \) can be compared with that obtained by the angle dispersive method.

Experimental

The block diagram of the present system for the white X-ray diffraction from a powder sample is shown in Fig. 1. The SSD is fixed and the X-ray tube is rotated to change the Bragg angle, because the SSD includes a Dewar vessel of about 30 litres. Although white X-ray diffraction can generally be completed by measurements at two or three fixed Bragg angles, our system has the usual goniometer which enables us to carry out measurements by the angle dispersive method also. This capability was useful in the measurement of \( I_{\text{wr}}(E) \).

As a source of the white X-rays, the continuous X-rays from a Cu tube operated at 40 kV and 16 or 20 mA were used. In order to avoid the effect of the \( K \) absorption edge of Ga, white X-rays ranging from 16 to 35 keV were used. The particle size of the GaP powder sample was less than 3 \( \mu \)m, so that primary extinction may be neglected.

The heights of the divergence slit and the receiving slit were both 4 mm. The horizontal divergence of the incident beam was \( 15^\circ \), the width of the receiving slit 0.3 mm and the camera length 185 mm. The limiting divergence of the Soller slit was 4.9°.

Measurements

(1) Integrated intensities and \( \mu_{r} \) of GaP

In a measurement of integrated intensities, it was not easy to estimate the background, because its shape was not as simple as in the case of the usual angle dispersive method, being due to the Compton scattering. The overall background was expressed by a power series in \( E \), the coefficients of which were determined by the least-squares method. The degree of the power series was chosen to be fourth or fifth in each measurement so that the shape of the background was most reasonable.

In the measurement of \( \mu_{r} \), a slice of GaP about 0.15 mm thick was put in front of the receiving slit. The value of \( \mu_{r} \) was estimated from equation (2) for each reflexion at a different energy. After several measurements, the energy dependence of \( \mu_{r} \) was found to be expressed by a power series in \( E \) in the calculation of \( F(hk\ell) \). Its energy dependence is shown in Fig. 2. In the range from 16 to 35 keV, \( \mu_{r} \) was approximately proportional to \( E^{-2.7} \).

(2) The energy spectrum of the white X-rays

The integrated intensity of the 220 reflexion of a GaP powder sample was measured at nine Bragg angles. The values of \( F(220) \) at nine relevant energies were calculated from equation (3), by the use of the temperature factors, \( B_{Ga}=0.875\ \text{Å}^{2} \) and \( B_{P}=0.816\ \text{Å}^{2} \), which were obtained by the usual angle dispersive method on the same sample. Then, from \( L(220) \) at nine energies \( I_{\text{wr}}(E) \) was estimated with equation (1).

Results

Integrated intensities of reflexions from 111 to 311 were measured at the Bragg angle of 6-65° and those from 311 to 531 at 12-70°. By the use of equation (4), the corrected relative structure factors were converted.
into the absolute structure factors without anomalous dispersion, $F_0^{\alpha}(hkl)$, included. The results are shown in Table 1, along with the structure factors, $F_m^{\alpha}(hkl)$, of the same sample obtained by the usual angle dispersive method with the monochromatized incident beam (Uno, Okano & Yukino, 1970). From the data measured at $6.65^\circ$, the values of the third column of Table 1 were directly obtained by minimizing $\langle \Delta Q(r)^2 \rangle$. In this case $B_{Ga}$ and $B_p$ were 0.253 Å$^2$ and 0.345 Å$^2$ respectively. These values were considerably different from those obtained by the angle dispersive method on the same sample. This fact implies that the scale factor was not reasonable, because it was estimated from only four reflexions. Therefore the scale factor of the data at $6.65^\circ$ was changed to give the same value of $F(311)$ as that obtained at $12.70^\circ$. The newly scaled structure factors are shown in the fourth column.

The values of $\log \left( \frac{|F_0^{\alpha}(hkl)|}{|F_0(hkl)|} \right)$ plotted against $\sin^2 \theta / \lambda^2$ in Fig. 3, are expressed by open circles when $F_0^{\alpha}(hkl)=F_m^{\alpha}(hkl)$ and by solid circles when $F_0^{\alpha}(hkl)=F_m^a(hkl)$, where $F_m^a(hkl)$ is the calculated structure factor of GaP without the thermal vibration and the anomalous dispersion.

As for $|F_0^a(222)|$, the 222 reflexion overlapped so much with the 311 reflexion that the estimated integrated intensity of the 222 contained a contribution from the tail of the 311, because the two reflexions were separated at the minimum point between them. From the figure, $|F_0^a(531)|$ appears to be too large. This seems to be due to the fact that the background was estimated to be so low in the highest-energy region that its integrated intensity was rather high. Except $F_0^a(222)$ and $F_0^a(531)$, the structure factors obtained by the energy dispersive method agree well with those obtained by the angle dispersive method. This means that the energy dispersive method with white X-rays can be used for determining structure factors, as well as the angle dispersive method with monochromatized X-rays.

Table 1. Comparison of structure factors of GaP obtained by the angle dispersive method, $F_0^{\alpha}(hkl)$, and the energy dispersive method, $F_0^a(hkl)$

| hkl | $|F_0^{\alpha}|$ | $\theta = 6.65^\circ$ | $|F_0^{\alpha}|$ | $\theta = 12.70^\circ$ |
|-----|----------------|----------------|----------------|----------------|
| 111 | 112.88 ± 1.35  | 115.14 ± 1.35  | 109.78 ± 0.16  | 108.00 ± 0.45  |
| 200 | 55.99 ± 0.28   | 58.22 ± 0.28   | 55.51 ± 0.46   | 54.99 ± 1.49   |
| 220 | 121.70 ± 0.57  | 125.00 ± 0.57  | 119.19 ± 0.97  | 119.00 ± 0.45  |
| 311 | 84.82 ± 0.34   | 90.20 ± 0.34   | 86.00 ± 0.29   | 86.00 ± 0.45   |
| 222 | 46.99 ± 1.04   | 49.00 ± 1.04   | 49.00 ± 0.99   | 49.00 ± 1.49   |
| 400 | 93.57 ± 1.28   | 94.08 ± 1.28   | 94.08 ± 0.70   | 94.08 ± 1.49   |
| 331 | 67.96 ± 0.29   | 69.45 ± 0.29   | 69.45 ± 0.97   | 69.45 ± 1.49   |
| 420 | 36.41 ± 0.05   | 36.63 ± 0.05   | 36.63 ± 0.73   | 36.63 ± 1.49   |
| 422 | 80.55 ± 0.86   | 81.97 ± 0.86   | 81.97 ± 0.57   | 81.97 ± 1.49   |
| 333 | 56.97 ± 0.99   | 58.05 ± 0.99   | 58.05 ± 0.50   | 58.05 ± 1.49   |
| 511 | 56.97 ± 0.99   | 58.05 ± 0.99   | 58.05 ± 0.50   | 58.05 ± 1.49   |
| 440 | 67.02 ± 2.32   | 69.42 ± 2.32   | 69.42 ± 1.72   | 69.42 ± 1.49   |
| 531 | 50.50 ± 0.71   | 54.44 ± 0.71   | 54.44 ± 0.96   | 54.44 ± 1.49   |

Discussion

Concerning white X-ray diffraction, it is said as usual that data at two or three Bragg angles are enough to obtain structure factors, so that this method is very convenient to carry out measurements under extreme experimental conditions, such as at low temperature. However, in our method of obtaining $I_w(E)$, data at nine Bragg angles were necessary. In order to improve our method it is desirable that $I_w(E)$ is measured directly by the SSD at very low tube current.

Being due to the geometrical conditions of the slit system, the measured reflexion contained X-rays of a certain range of energy. Therefore, the measured intensities were the integrals of the contributions from...
such X-rays. However, in our measurement, structure factors were obtained relative to $F(220)$, so that they would be free from errors due to the above-mentioned energy breadth.

In the present work, $I_{wr}(E)$ could fortunately be obtained from $L(220)$ of the sample material. Therefore, it was not necessary in principle to measure $\mu_s(E)$ for the sample, because $I_{wr}(E)/\mu_s(E)$ could be obtained from $L(220)$ at various energies and could be used for the estimation of $F_s(hkl)$ from $L(hkl)$.

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