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Abstract

Multiple electron scattering between weak beams has been used as the basis for a simple method to determine the absolute polarity of some non-centrosymmetric crystals. For crystals with the sphalerite structure many orientations have been found in which small departures from centrosymmetry produce large effects on the convergent-beam diffraction patterns (microdiffraction). The effects are reasonably independent of thickness and so can be analyzed qualitatively without the use of computers.

Introduction

The ease with which high-quality convergent-beam microdiffraction patterns can be obtained with some modern electron microscopes has made this technique promising for studies of small crystals, microphases and inclusions in materials science and mineralogy. The possibility of focusing the beam on a small area without contamination also greatly simplifies specimen preparation in many cases.

Since, for the usual conditions of strong multiple scattering, Friedel's law does not apply to electron diffraction (Goodman & Lehmpfuhl, 1968), convergent-beam electron diffraction has become a technique of increasing interest for the determination of crystal symmetries and the phases of structure factors (Goodman & Johnson, 1977; Buxton, Eedes, Steeds & Rackham, 1976; Tanaka, Saito & Watanabe, 1980). Attention has mainly been focused on systematic row orientations or directions exactly along or close to low-index zone axes.

The zone-axis case is attractive because much information may be obtained from a single exposure. Apparent mirror planes and centrosymmetry should, however, be tested more carefully, because a weak asymmetry may disappear owing to the exitation of many strong irrelevant reflections. In addition, difficulties may arise because low-index zone axes are very sensitive to thickness, small changes of incident-beam direction and surface boundary effects. These problems have been discussed carefully in the above mentioned work of Buxton et al. The systematic row orientation in some cases may also be unnecessarily complicated for structure-factor phase determination, because in the interpretation one has to rely on reflections for which the Bragg conditions are far from fulfilled. Reflections away from the Ewald sphere may create severe difficulties for a simple interpretation even in thin crystals. In order to observe the breakdown of Friedel's law it is necessary to excite two or more beams in addition to the central beam. In addition, the Cowley-Moodie (1962) polynomial expression for n-beam scattering allows a simple interpretation based on quasi-kinematical concepts if all excitation errors are zero. This is not possible for \( n > 2 \) in the systematic case. Thus we have sought non-systematics cases where several weak beams are excited all with zero excitation error in order to test their sensitivity to the loss of symmetry elements.

In the present study of GaAs we have used the coupling between the weak 200 reflection and weak odd-index reflections. Situations with the 200 and 200 reflections respectively at Bragg position were compared. The results have been compared with similar convergent-beam patterns from germanium. These two crystals are very similar except for the fact that the [200] and the [200] directions are equivalent in Ge.

Experiment

The specimens were prepared by grinding the crystals in a mortar and the fine grains were collected on a holey carbon film. Convergent-beam diffraction patterns were obtained with a Philips EM400 electron microscope operating at 100 kV.

From convergent-beam patterns exactly along or close to the [011] zone axis, it was difficult to get a decisive conclusion with respect to whether GaAs has a mirror plane parallel to the (200) planes, although there is no doubt that it is possible by careful choice of thickness, illuminated area and precise adjustment of the incident-beam direction.

By tilting the specimen about \( 10^\circ \) or more in the (200) plane many situations could be observed with a very large difference in the features of the 200 and 200 reflections when the Bragg condition for the reflection under consideration was fulfilled, and simultaneously...
two weak odd-index reflections were at the Bragg reflecting position. Fig. 1 shows an example. In Fig. 1(c) the Bragg condition is fulfilled for the 200, \( \bar{111} \bar{1} \) and 911 reflections and in Fig. 1(d) for 200, \( \bar{111} \bar{1} \) and 911. In the latter case the three reflections seem to scatter constructively into the 200 reflection, with particularly high intensity where the two sharp lines cross each other, whereas in the first case (c) there is reduced intensity along the lines corresponding to the Bragg reflecting position for \( \bar{111} \bar{1} \) and 911. This suggests that the scattering from those two reflections interferes destructively with the 200 reflection. Figs. 1(e) and (f) show similar diffraction conditions for Ge. Here of course there is no difference for the two cases in accordance with the fact that there are mirror planes parallel to the (200) plane. The intensity is increased considerably where the two bright lines cross each other, similar to the right hand case for GaAs.

Fig. 2 shows the same diffraction conditions in a thicker GaAs crystal. In Fig. 2(a) we notice that the features are mainly the same as for the thinner crystal with a gap between the dark lines whose width seems to be independent of thickness. The gap width is sensitive to the value of the 200 structure factor and may be used for the determination of the magnitude of the structure factor and so to the dopant concentration. This effect is somewhat related to the gap between intersecting Kikuchi lines (Gjønnes & Höier, 1971) which has been used for accurate structure-factor determination (Terasaki, Watanabe & Gjønnes, 1979), and was explained as an increase of the extinction distance towards infinity. In Fig. 2(b) the features are different from the thin-crystal case, but even for this larger thickness (greater than 2000 Å) the intensity on the right (Fig. 2b) is still usefully larger than that on the left (Fig. 2a).

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Fig. 1. (a) Example of the diffraction conditions. (b) Schematic drawing showing the important reflections and the scattering paths from the central beam to the 200 reflection. (c) and (d) GaAs with 200 and 200 reflections at Bragg position, respectively. (e) and (f) Ge with diffraction condition similar to (c) and (d).
Fig. 3 shows two other examples for other directions of incidence in a rather thin GaAs crystal. Similar effects have also been observed in cubic ZnSe and ZnS.

**Interpretation**

The structure factors for the reflections close to the Ewald sphere in Fig. 1, i.e. 200, 911 and 111,1, are quite small. Extinction lengths for all of them are more than 4000 Å at 100 kV in GaAs. The situation in Ge is similar except for the fact that the 200 reflection is extinguished. Therefore, for crystal thicknesses up to a few hundred ångströms the phase change due to increasing thickness is negligible for such weak reflections. Hence the main factors affecting the phase when the reflections are close to the Bragg position are the relative phases of the structure factors and the phase change of $-\pi/2$ associated with each scattering process. The phase change in the thin-crystal approximation for $n$-times scattering can then be written:

$$\omega = -\frac{n\pi}{2} + \sum_{i=1}^{n} \omega_i$$  \hspace{1cm} (1)

where $\omega_i$ are the phases of the structure factors. This simple expression can be justified using the polynomial expression for dynamical scattering given by Cowley & Moodie (1962) with excitation errors equal to zero.

Fig. 2. The same diffraction conditions as in Fig. 1 for a thicker GaAs crystal. (a) corresponds to Fig. 1(c) and (b) to Fig. 1(d).

Fig. 3. Diffraction pattern from GaAs showing two four-beam situations at the same exposure. (a) Schematic drawing showing the important reflections with 200 at the Bragg position. (b) Diffraction pattern with 200 at the Bragg position. (c) and (d) Enlarged diffraction patterns corresponding to (a) and (b), respectively. The upper crosses correspond to incident-beam directions for which the 200-, 951- and 751-type reflections are at the Bragg position, and the lower ones to 200-, 931- and 731-type reflections at the Bragg position.
We consider first the case of Ge. Choosing the origin at the centrosymmetric position with the nearest atoms at \(1/8 \ 1/8 \ 1/8\) and \(1/8 \ 1/8 \ 1/8\), we may write the structure factors for the odd-index reflections as

\[ F_{h+k+l=2n+1} = 8f_{\text{Ge}} \cos \left[ \frac{\pi}{4}(h+k+l) \right]. \]

In particular, we have

\[ F(91\bar{1}) = F(9\bar{1}1) = 4\sqrt{2}f_{\text{Ge}} \]

\[ F(11.1.1) = F(\bar{1}1.1.1) = -4\sqrt{2}f_{\text{Ge}}. \]

The coupling between the two odd-index reflections with reciprocal vector \([20,0,0]\) is negligible. Estimates choosing the Debye-Waller factor to be \(0.60 \AA^{-2}\) give: \(F_{20.0.0} = 1/7 \ F_{11.1.1}\). There are hence essentially only two scattering paths from the central beam to the 200 reflection, namely: \(000 \rightarrow \bar{1}1.1 \rightarrow 200\) and \(000 \rightarrow 91\bar{1} \rightarrow 200\), as indicated in Fig. 1(b). From (1) we then obtain a phase change of zero for both paths. The scattering into the 200 coordinate will therefore interfere constructively in accordance with the observations of Fig. 1(f). The situation is the same in Fig. 1(e) with the \(\bar{1}1.1.1\) and 91\bar{1} reflections strongly excited.

In GaAs the structure factors of the odd-index reflections and the reflections of the type \(h+k+l=4n\) are not much different as compared to Ge, and they will be assumed to be the same. But, in addition, the reflections with \(h+k+l=4n+2\) are now excited, although weak. With the origin similar to that chosen in Ge, placing Ga at \(1/8 \ 1/8 \ 1/8\) and As at \(1/8 \ 1/8 \ 1/8\), the structure factors of these reflections can be written

\[ F_{h+k+l=4n+2} = 4 \left\{ f_{\text{Ga}} \exp \left[ 2\pi i \left( -\frac{1}{8}h - \frac{1}{8}k - \frac{1}{8}l \right) \right] \right. \]

\[ \left. + f_{\text{As}} \exp \left[ 2\pi i \left( \frac{1}{8}h + \frac{1}{8}k + \frac{1}{8}l \right) \right] \right\}. \]

We may write \(f_{\text{As}} = f + \Delta\) and \(f_{\text{Ga}} = f - \Delta\), where \(\Delta\) is positive, giving

\[ F_{200} = 8\Delta \exp \left( -\frac{\pi}{2} i \right) \]

\[ F_{2\bar{1}00} = 8\Delta \exp \left( \frac{\pi}{2} i \right). \]

As compared to Ge there is now a third path of scattering into the 200-type reflection (the direct path) and the phase change for this path is, according to (1),

\[ 000 \rightarrow 2\bar{1}00 = -\frac{\pi}{2} + \omega_{2\bar{1}00} = -\pi \]

\[ 000 \rightarrow 200 = -\frac{\pi}{2} + \omega_{200} = 0. \]

Hence the direct scattering into 2\bar{1}00 is \(\pi\) out-of-phase with the scattering over the two other paths, whereas all three paths scatter with the same phase into 200. In the lower cross of Fig. 3(c) with the 200, 93\bar{1} and 73\bar{1} strongly excited (200, 93\bar{1} and 73\bar{1} in Fig. 3(d)), the phase changes for scattering over the odd-index reflections are also zero. For the upper cross, however, with 200, 951 and 751 the phase changes for scattering over the odd-index reflections are \(\pi\). Therefore, there is constructive interference on the opposite side in the latter case. All three cases analyzed with the atomic coordinates given are consistent with the absolute orientation of the crystal relative to the diffraction patterns of Figs. 1–3 shown in Fig. 4.

A question which may be raised in connection with such a simple interpretation is the effect of reflections not taken into account. Certainly, many reflections must be included in a quantitative treatment, particularly the strong reflections along the 200 row. If we look at this systematic row separately the effect of the other beams along the row is a decrease of the extinction length for the 200-type reflection, but its phase remains the same in the thin-crystal approximation. The interpretation as far as the phase of the 200-type asymmetry seems therefore not to be affected by the many-beam interaction.

Fig. 4. (a) The sphalerite structure. (b) The absolute orientation of the crystal in the [011] projection relative to the diffraction patterns of Figs. 1–3. Small circles represent Ga and large circles As.
Conclusion

The present study has shown that small deviations from centrosymmetry can clearly and easily be observed by taking advantage of the strong coherent multiple scattering normally present in convergent-beam electron diffraction. The direction of the asymmetry in GaAs can also be determined very simply, without use of computers, when only two or three weak reflections are close to the Bragg reflecting position.

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References