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Determination of Crystal Symmetry from Electron Channelling Patterns

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Abstract

The application of selected area channelling patterns in crystal symmetry determination has been investigated. In addition to rotation axes and mirror planes diffraction effects have been observed which may be ascribed to violation of Friedel's law. It has thus been possible for the first time with this technique to distinguish uniquely between centrosymmetric and non-centrosymmetric point groups. This is demonstrated with examples taken from the cubic and the hexagonal crystal systems, of which some show very detailed zone-axis absorption HOLZ patterns. Owing to the large tilt angle represented in each diagram the directions of double scattering may easily be localized. It is shown that this may be utilized in determination of the extinctions and the space group. The sensitivity to deviation from centrosymmetry is discussed and found to be somewhat less than for the convergent-beam technique. Crystal sizes from micrometres to bulk may be used. The strength of the channelling method is its simplicity and in particular the possible use of bulk specimens which may also be directly studied by other techniques, for example by X-rays.

Introduction

When the back-scattered electron intensity is registered as a function of the incident beam direction in a transmission or scanning electron microscope, a selected area electron channelling pattern is obtained. These patterns, which are due to anomalous absorption effects in the forward-scattered Bragg beams, have so far been used mainly to determine lattice parameters and crystallographic orientations and to study different types of deformations [see, for example, Schulson (1977), Joy, Newbury & Davidson (1982), and references therein]. However, the patterns also provide more detailed structure information. In recent work (Marthinsen & Høier, 1986; Marthinsen, 1986) many-beam dynamical diffraction phenomena in relation to phase information have been investigated. It was found that information on the invariant sum of structure-factor phases involved in a three-beam interaction could be obtained experimentally in centrosymmetric as well as in non-centrosymmetric crystals.

In this work we are concerned with another possible application of selected area channelling patterns (SACP) in structure studies. As lines belonging to several layers in reciprocal space are observed in a single exposure, the patterns may be utilized to determine the crystal symmetry. Although this fact has been referred to in the literature (*e.g.* Joy, 1974), no systematic studies have so far been performed. The main purpose of the present work is to investigate in general the possible use of channelling patterns for determinations of point-group symmetry and extinctions and thus the crystal space group. The method will to some extent be compared with a transmission diffraction technique, convergent-beam electron diffraction (CBED), which is a well established technique for the determination of crystal symmetry (*e.g.* Goodman, 1975; Buxton, Eades, Steeds & Rackham, 1976; Steeds & Vincent, 1983; Tanaka, Sekii & Nagasawa, 1983).

In the present studies we have focused on the cubic crystal system with additional examples from the hexagonal and the trigonal systems. It has been of particular interest to see whether non-centrosymmetric groups may be distinguished from the centrosymmetric ones. Some results have previously been given by Høier & Marthinsen (1986).

Experimental

The experiments were carried out in a JSM-840 scanning electron microscope (SEM). A rotation/tilt holder was used and the selected area was typically 10 μm or less. The experimental technique is described by Joy, Newbury & Davidson (1982).

Specimens of Si, FeS_2, GaSb, GaAs, Sb and SiC were investigated. The Si, GaSb and GaAs specimens were prepared in the standard way. The other specimens had naturally grown surfaces or cleavage surfaces of sufficient quality and were not subjected to any particular preparation. The small illumination area of the incident beam made it possible to locate areas on the specimens of good-enough condition to obtain channelling patterns of sufficient quality. In all the patterns presented below the incident beam

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direction was approximately parallel to the surface normals and also to the actual zone axes examined.

Point-group determination

The centre of intersections between several line pairs in an electron channelling pattern corresponds to a crystallographic zone axis. As proposed, for example, by Steeds & Vincent (1983) for CBED patterns, a good way of determining the crystal point group is to locate prominent zone axes and then examine the symmetry properties of these zone-axis patterns. This procedure will also be followed in the present SACP studies.

An electron channelling pattern from a [001] Si specimen is shown in Fig. 1(*a*). Mirror planes are easily recognized in the middle of the 220 and 400 bands. It is therefore clear that the [001] zone-axis pattern has 4*mm* symmetry as expected from the structure of Si. This symmetry may also be deduced from the fine details near the zone axis as shown in Fig. 1(*b*). The very detailed weak lines observed are the absorption HOLZ (higher-order Laue zone) lines (Marthinsen & Høier, 1986) and thus the channelling analogue to the similar type of lines observed in transmission diffraction patterns. The HOLZ line pattern changes rapidly with small changes in the acceleration voltage of the microscope. This is demonstrated by comparing Figs. 1(*b*) and (*c*). The 4*mm* symmetry is, however, retained.

An Si [111] pattern is shown in Fig. 2(*a*). Careful inspection reveals 3*m* symmetry with mirrors along the 220 bands. In this case as well the actual symmetry may be observed in the zone-axis HOLZ lines alone (Fig. 2*b*).

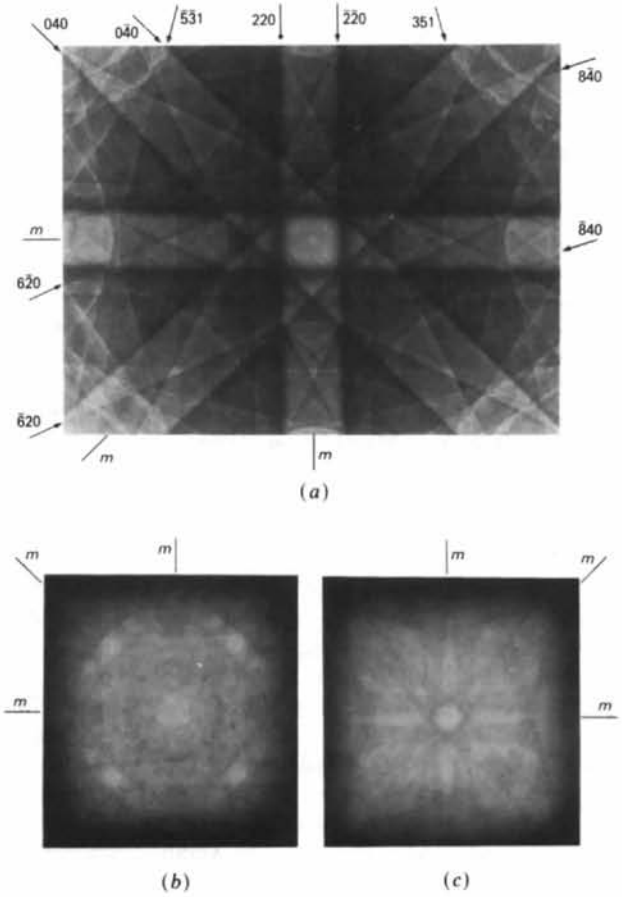


Fig. 1. (*a*) SACP from [001] zone in Si, 4*mm* symmetry (25 kV). (*b*) HOLZ pattern from the [001] zone, 25 kV. (*c*) HOLZ pattern, 20 kV.

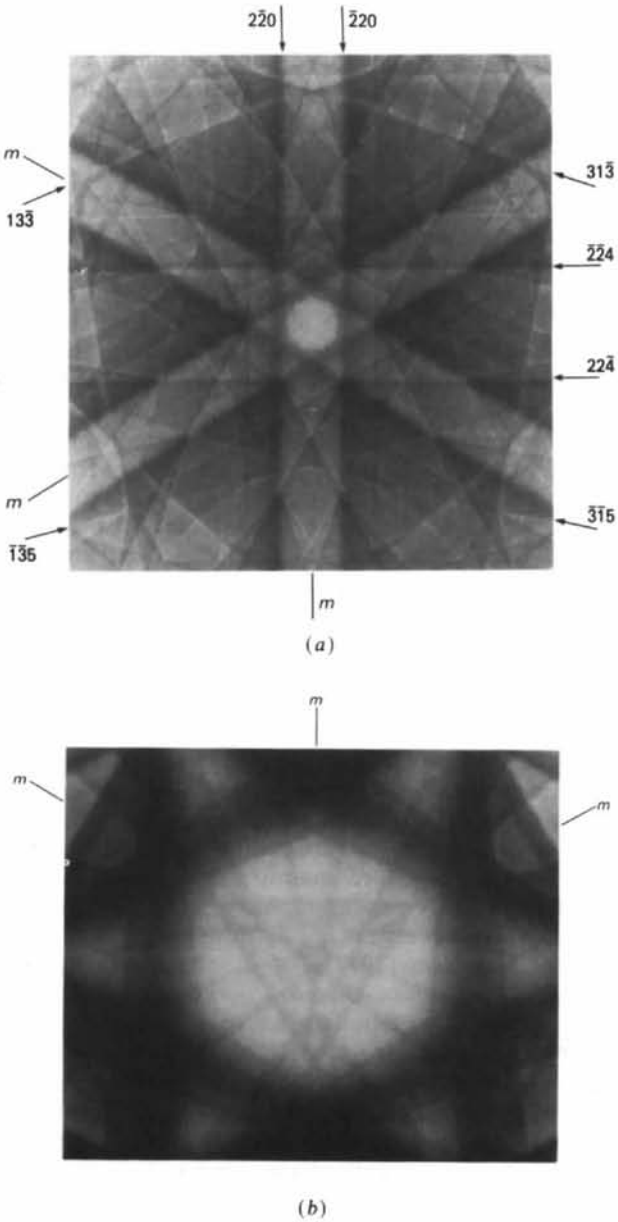
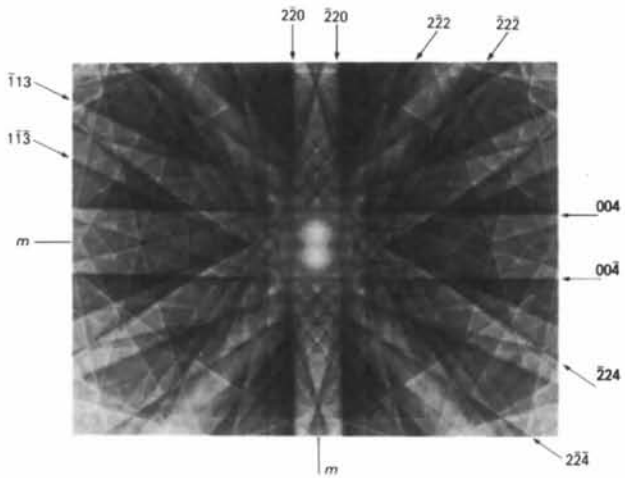


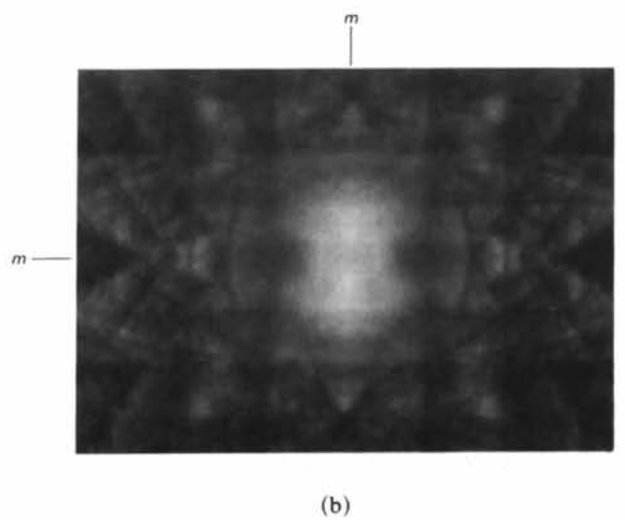
Fig. 2. (*a*) SACP from [111] zone in Si, 3*m* symmetry (40 kV). (*b*) HOLZ pattern, 22 kV.

The third high-symmetry zones of Si are the ⟨110⟩ zones. In the pattern in Fig. 3(*a*) mirror planes are observed in the middle of the 004 and 220 bands and the symmetry 2*mm* results. The central part of Fig. 3(*a*), *i.e.* the area near the zone axis, is shown in (*b*). No HOLZ lines are discerned in this pattern, but the complicated and regular diffuse intensity pattern in the centre still reveals the 2*mm* symmetry.

Other zones with particular symmetry properties in Si are the ⟨*uv*0⟩ and ⟨*uuv*⟩ zones situated along the 400 and 220 bands, respectively. As a result of the mirror planes in the middle of these bands, they all have mirror symmetry. All these observations uniquely determine the point group $m\bar{3}m$, in accordance with the structure of Si with point group $m\bar{3}m$ and the space group $Fd\bar{3}m$.



(a)



(b)

Fig. 3. (*a*) SACP from [110] zone in Si, 2*mm* symmetry (25 kV). (*b*) Near zone-axis pattern, 20 kV.

The next example is FeS_2 ($m\bar{3}$, $Pa\bar{3}$). In Fig. 4 the [001] zone-axis pattern from FeS_2 is shown. Although diffuse and with far less details than the preceding patterns for Si, the pattern in Fig. 4 clearly shows 2*mm* symmetry with mirror planes in the 200 bands. As opposed to the [001] pattern of Si there are no mirrors in the 220 bands. This fact, which is responsible for the reduction to 2*mm* symmetry, is, for instance, seen in the bright area near the zone axis. It is also seen if one focuses on the lines shown by the arrows in the figure. It further follows from this pattern that the ⟨*uv*0⟩ zones, situated along the 200 bands, have mirror symmetry, whereas the ⟨*uuv*⟩ zones, situated along the 220 bands, lack this symmetry. This is in correspondence with the correct point group $m\bar{3}$ for this crystal. In this and the remaining examples below we have only examined selected zone axes. In this way we have not obtained sufficient information to identify uniquely the point groups in all the cases. However, the examples illustrate the potential of electron channelling patterns to identify different point-group elements.

From the results above it may be concluded that we can distinguish between the two Laue classes of the cubic system. The question is whether we can also distinguish between two point groups within the same Laue class. This may be seen by comparison with patterns from GaSb which has a strong non-centrosymmetric structure with the same Laue symmetry as Si. The point group is $\bar{4}3m$ and the space group $F\bar{4}3m$. A [001] zone-axis pattern is shown in Fig. 5(*a*). Deviation from mirror symmetry in the 020 bands is most clearly seen near the ⟨105⟩ zones. The lines to be compared are shown by arrows. The details in one of these zones are shown in Fig. 5(*b*). We notice in particular that the lines 51$\bar{1}$ and 5$\bar{1}\bar{1}$, for

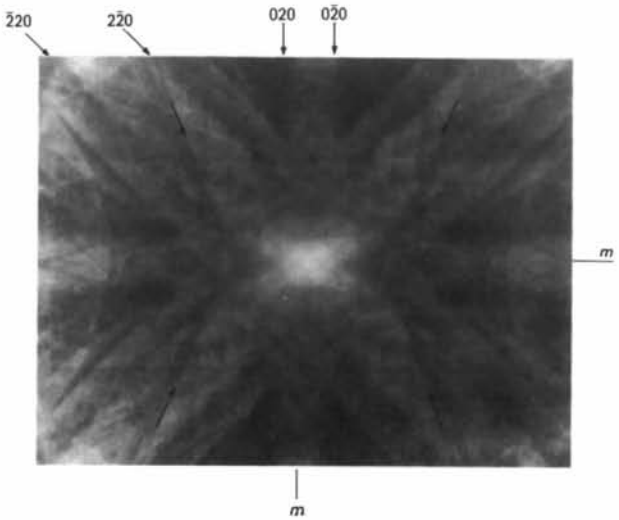
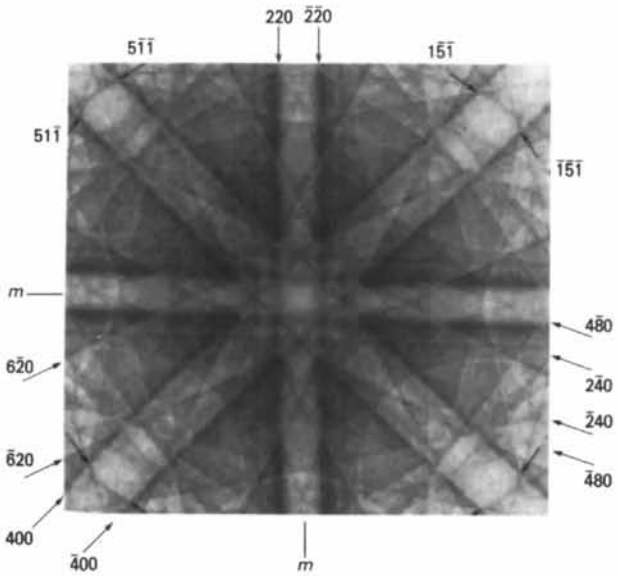


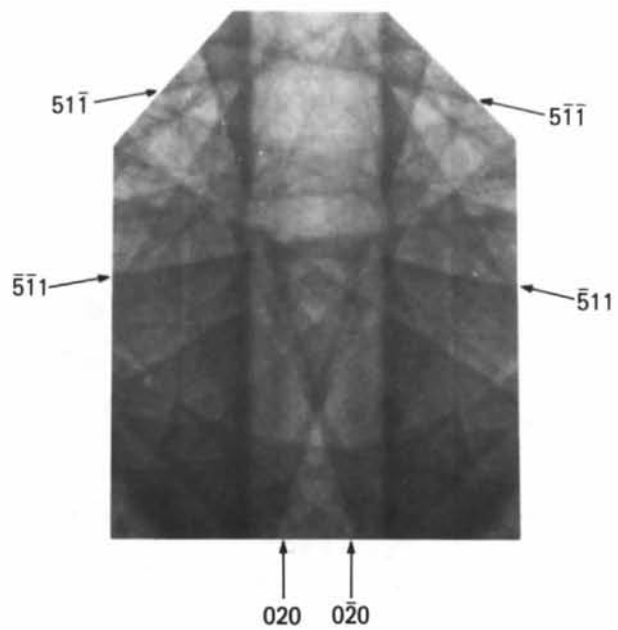
Fig. 4. A [001] zone-axis pattern from FeS_2, 2*mm* symmetry. Mirror planes in the 020 bands.

Table 1. *Zone-axis symmetries in electron channelling patterns from cubic crystals*

Specimen	Laue class	Point group	⟨100⟩	⟨111⟩	⟨110⟩	⟨*uv*0⟩	⟨*uuv*⟩	[*uvw*]
FeS_2	$m\bar{3}$	$m\bar{3}$	$2mm^*$	3		m^*		1^*
		23	2	3		1		1
Si	$m\bar{3}m$	$m\bar{3}m$	$4mm^*$	$3m^*$	$2mm^*$	m^*	m^*	1^*
GaSb		$\bar{4}3m$	$2mm^*$	$3m$	m	1^*	m^*	1^*
		432	4	3	2	1	1	1



(*a*)



(*b*)

Fig. 5. (*a*) [001] zone-axis pattern from GaSb, $2mm$ symmetry. Arrows show lines with asymmetric contrast in the ⟨105⟩ zones, giving mirror planes only in the 220 bands. (*b*) A close-up view of the [105] zone.

instance, are observed with different contrast inside the 020 band. It is this effect which destroys the mirror symmetry and accordingly distinguishes this pattern from the [001] pattern of Si. The asymmetry may be considered as a breakdown of Friedel's law in a broad sense since the $5\bar{1}\bar{1}$ reflection is equivalent crystallographically to the $\bar{5}1\bar{1}$ reflection in GaSb. In this case the ⟨*uuv*⟩ zones have mirror symmetry whereas the ⟨*uv*0⟩ zones do not, in accordance with the point group $\bar{4}3m$.

The intensity anomalies observed near the ⟨105⟩ zones are due to non-systematic many-beam interactions, but cannot be explained by any of the existing theoretical expressions for the electron channelling contrast where the different Bloch waves in general are treated as independent. The oscillating thickness-dependent contributions coming from the coupling terms between the Bloch waves are generally believed to integrate out and are therefore omitted. However, to explain the observed effects in Fig. 5 it is necessary to include these terms (Marthinsen, Anisdahl & Høier, 1987; Marthinsen & Høier, 1988*b*).

The results obtained for Si, FeS_2 and GaSb have been summarized in Table 1, where the zone axes we have examined and the corresponding observed zone-axis symmetries are indicated with asterisks (*). For completeness the zone-axis symmetries to be expected from the remaining high-symmetry zones of these crystals as well as the additional cubic point groups and the corresponding expected zone-axis symmetries in these cases are included. These symmetries will be observed, given that violation of Friedel's law can indeed be observed in all cases. From Table 1 we see that all the cubic point groups can uniquely be identified and distinguished from the other ones. The zone-axis symmetries indicated in Table 1 correspond to the whole-pattern symmetries in CBED patterns (*e.g.* Buxton, Eades, Steeds & Rackham, 1976).

To test the sensitivity of the SACP method to detect small deviations from centrosymmetry we have included GaAs. GaAs has the same point and space group as GaSb, but since the two atomic types Ga and As differ by only two in atomic number, the structure is only slightly non-centrosymmetric. In accordance with the point group, the [001] zone-axis pattern, shown in Fig. 6, should have $2mm$ symmetry. However, close examination of this pattern gives no factual evidence to say that mirror symmetry is violated in the 200 bands. The observed [001] zone-axis

symmetry is hence $4mm$, which is not in accordance with the structure of GaAs. This means that the diffraction effects which made it possible to determine the correct non-centrosymmetric point group for GaSb are not sensitive enough to detect this small deviation from centrosymmetry with the present instrumental possibilities.

So far only cubic crystals have been considered. However, to see whether point-group elements may also be obtained from crystals of lower symmetry, we have in addition investigated a hexagonal crystal, SiC ($6mm$, $P6_3mc$), and a trigonal crystal, Sb ($\bar{3}m$, $R\bar{3}m$). The point group and the space group are given in parentheses. The [001] pattern of Sb is shown in Fig. 7. The symmetry is $3m$, which is in accordance with the point group, $\bar{3}m$. However, to identify uniquely the correct point group or Laue class, symmetry properties of other zone axes would have to be included.

The [001] zone-axis pattern of SiC at an acceleration voltage of 30 kV is reproduced in Fig. 8(a). In Fig. 8(b) the same zone-axis pattern is shown at 40 kV. HOLZ patterns with previously unobserved details are here, as in Fig. 1, seen in the bright central areas of these figures. Both figures reveal the correct symmetry of $6mm$. However, in this case as well we need additional information from other zone axes to distinguish between the two possible point groups, $6mm$ and $6/mmm$.

Space-group determination

Once one has determined the crystal point group, or at least the Laue class, the next step in a structure determination is to identify the extinctions. However, it is a common experience in electron diffraction that this task is complicated by double scattering effects; diffraction spots may appear in kinematically forbidden positions. But in electron channelling patterns this problem can be eliminated. The contrast variation in a line for various diffraction conditions is directly obtained by investigating it along its length. Directions of strong many-beam interactions may thus be localized and excluded.

To determine the space group we need the extinctions in addition to the point group. To show that the extinctions can in fact be determined from channelling patterns we shall reinvestigate some of the patterns for that purpose, starting with Si. Inspecting Figs. 1, 2 and 3, one finds easily that the indices are either all odd or all even. This is in accordance with the reflection conditions for a face-centred cubic (f.c.c.) lattice. A selection of indices is indicated in the figures. In addition, it is found that the condition $h+k+l \neq 4n+2$ must be fulfilled. Lines of the type 200, 600, 420 and 622, for example, are systematically absent. Nevertheless, small segments of the 002 and 006 lines are seen near the [110] zone in Figs. 3(a) and (b). Some of these segments, which originate from strong many-beam interactions, are indicated by arrows. Another type of line which contradicts the reflection conditions is the 222 line. Although this line corresponds to a reflection which is kinematically forbidden, it appears with strong contrast along its entire length. This line is also due to strong many-beam interactions and is discussed thoroughly elsewhere (*e.g.* Spencer, Humphreys & Hirsch, 1972; Marthinsen & Høier, 1986).

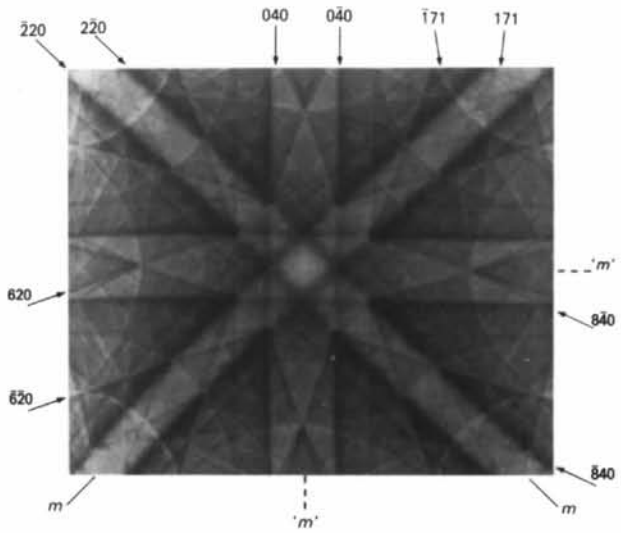


Fig. 6. [001] zone-axis pattern from GaAs. Apparently $4mm$ symmetry.

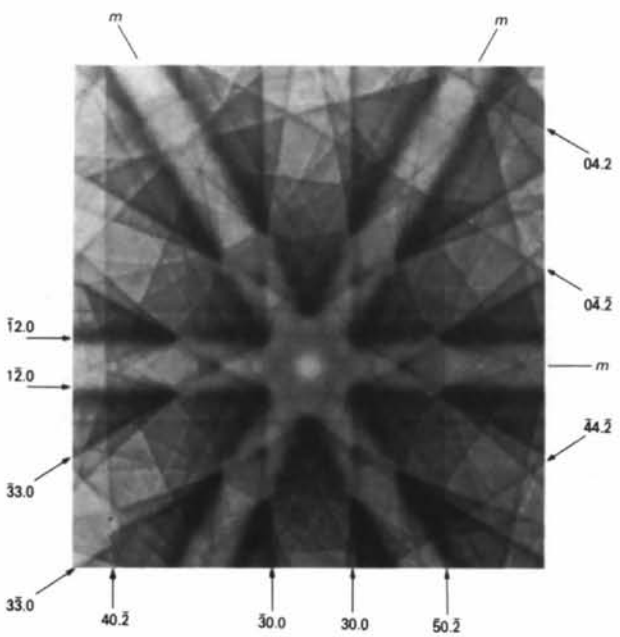
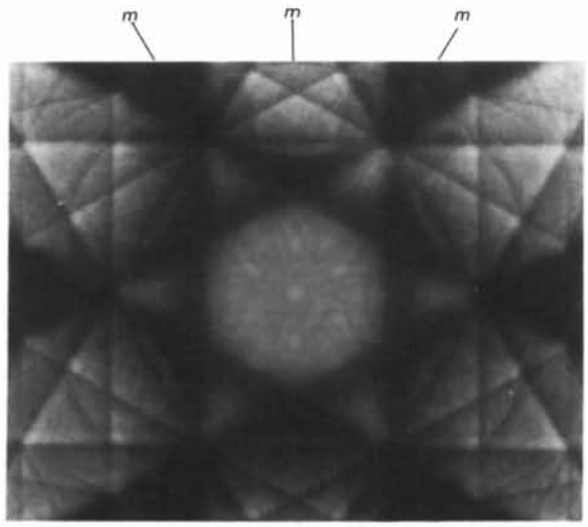


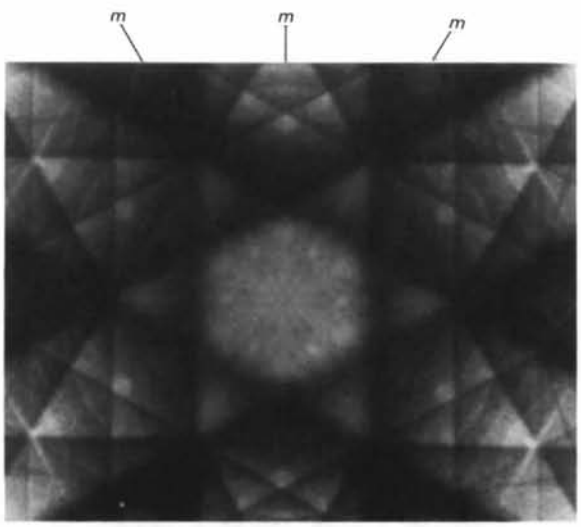
Fig. 7. [001] zone-axis pattern from Sb, $3m$ symmetry.

The reflection conditions found for Si lead to the extinction symbol *Fd*-- (*International Tables for Crystallography*, 1983). Combined with the point group $m\bar{3}m$, this uniquely identifies the space group as $Fd\bar{3}m$ (no. 227) which is the correct one for Si.

Turning to GaSb, one easily identifies the general reflection conditions which correspond to a f.c.c. lattice. But, as opposed to Si, reflections of the type $h+k+l=4n+2$ are not systematically absent. As seen from Fig. 5(*a*), the 200 as well as the 420 lines may, even though they are weak, be observed along their entire length. Combining these results with the point group $\bar{4}3m$, one obtains the space group $F\bar{4}3m$ (no. 216).



(*a*)



(*b*)

Fig. 8. [001] zone-axis patterns from SiC, 6*mm* symmetry. (*a*) 30 kV, (*b*) 40 kV.

For GaAs the same reflection conditions apply as for GaSb. The extinctions which are caused by the f.c.c. lattice may be found relatively easily. However, one may erroneously be led to conclude that the reflections for which $h+k+l=4n+2$ are absent as found in the Si case. Because of the similarity with the diamond structure ($Fd\bar{3}m$), the reflections of the type $h+k+l=4n+2$ are very weak. But careful inspection of available channelling patterns from GaAs has still revealed lines corresponding to such reflections. There are three possible space groups which match the reflection conditions and the Laue symmetry ($m\bar{3}$) found from the SACP patterns in this case. These are $F432$ (no. 209), $F\bar{4}3m$ (no. 216) and $Fm\bar{3}m$ (no. 225), of which no. 216 is the correct one for GaAs.

Let us finally consider Sb. As seen from Table 3.2 of *International Tables for Crystallography* (1983), the indices indicated in Fig. 7 match the reflection conditions $-h+k+l=3n$ for general reflections $hk.l$ and $h+l=3n$ for $h\bar{h}.l$ reflections. There are three space groups, $R32$ (no. 155), $R3m$ (no. 160) and $R\bar{3}m$ (no. 166) with the Laue class $\bar{3}m$ which match these reflection conditions. Sb has the space group $R\bar{3}m$.

Discussion and concluding remarks

We have in the present work shown that electron channelling patterns may profitably be used to identify crystal point- and space-group elements. It is found that *n*-fold rotation axes and mirror planes can easily be detected. When HOLZ lines are present, these symmetry elements may be found from the HOLZ pattern alone, as shown for Si and SiC. By combining symmetry properties of different zone axes the crystal system and the Laue class can be determined. In addition, we have shown, using GaSb as an example, that SACP patterns may reveal the absence of an inversion centre. The crystal point group can thus uniquely be specified. However, for this purpose it is found that the SACP method has some limitations. In patterns from GaAs, which is only weakly non-centrosymmetric, we did not manage to disclose any violation of Friedel's law.

Practical problems may arise when zone axes with large angular differences have to be studied. This is partly due to the relatively limited angular range of a single pattern, but also to the fact that good-quality zone-axis patterns are only obtained when the axis of interest does not deviate too much from the surface normal. An asymmetry may appear across individual bands for tilted crystals, thereby lowering the actual symmetry (Pirouz, 1974). This problem can be tackled by preparing surfaces of the specimen with the desired surface normals.

Space-group determination depends on a correct deduction of the reflection conditions. In channelling patterns these must be found from systematic line absences. As exemplified by Si, GaSb and Sb, we believe that the extinctions may be determined with relative ease. Erroneous conclusions may occur in cases where certain reflections are very weak, as pointed out for reflections of the type $h+k+l=4n+2$ in GaAs. Another point which may affect a correct determination of the reflection conditions is strong dynamical many-beam interactions which imply the presence of kinematically forbidden lines. This problem may be eliminated by locating diffraction conditions where these effects play no or a minor role. When the reflection conditions and the point group are determined, the space group is uniquely identified. In those cases where only the Laue class and the reflection conditions are specified, a set of possible space groups is determined.

However, a problem which may complicate indexing the patterns, when applying this method to unknown crystals, is that the origins of line absences, whether from Bravais lattice or lattice translation effects, are not known (*cf.* Dingley & Baba-Kishi, 1986). This is a practical problem which may be handled by trial and error. To do so, available computer simulations of the patterns which may be obtained for any crystal system and Bravais lattice may be used as assistance.

Compared with convergent-beam techniques electron channelling has clear limitations in structure studies, but also some obvious advantages. When only very small crystals are studied, CBED is the only alternative with its high-quality patterns and possibility of determining whole-pattern bright-field and dark-field symmetries and in addition utilizing the so-called Gjønnes–Moodie lines (*e.g.* Steeds & Vincent, 1983; Tanaka *et al.*, 1983; Gjønnes & Moodie, 1965). The sensitivity to non-centrosymmetry is very good, making it possible, as opposed to the SACP technique at the present stage of experimental development, to determine experimentally the correct point group of GaAs, for example (Buxton *et al.*, 1976). The method, which is well established, may, however, imply careful specimen preparation as only very thin crystals can be investigated (thickness up to some thousands and lateral resolution down to some tens of ångströms).

The channelling method, on the other hand, is available in most scanning and transmission electron microscopes and areas down to some micrometres across in a bulk specimen may be studied. Because this is a back-scattering technique the surface has to be deformation free, which can be achieved by polishing methods, cleavage or natural growth. The specimen preparation is accordingly simpler than in the transmission case. One advantage of the method is the possible use of bulk specimens which afterwards may be investigated without modification by other experimental techniques, as, for example, with X-rays. As for the resolution in the patterns this may be further improved by better instrumentation and especially use of image processing systems.

In addition to symmetry information, both lattice parameters (Høier, 1969; Walker & Booker, 1982) and structure-factor phase information can be obtained from the patterns. In the latter case it has recently been shown that structure-factor phase invariants may be determined in centrosymmetric as well as non-centrosymmetric cases (Marthinsen & Høier, 1986; Marthinsen & Høier, 1988*a*).

An alternative to the electron channelling method in obtaining symmetry information from bulk crystals in a scanning electron microscope is the use of electron back-scattering patterns (EBSP) (Dingley & Baba-Kishi, 1986). The advantage of this method is a wider angular range of the diffraction patterns and a smaller area probed by the incident beam. However, the disadvantage of the EBSP, as compared with the selected area channelling patterns, is that the pattern quality is generally poorer. Zone-axis patterns with as many details as, for example, in Figs. 1(*b*) and (*c*) and Fig. 6 seem unobtainable at present. Moreover, this means that the EBSP's ability to reveal departure from centrosymmetry is limited. Although this possibility has been suggested, only centrosymmetrical examples have so far been reported (Dingley & Baba-Kishi, 1986).

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On the Breakdown of Friedel's Law in Electron Backscattering Channelling Patterns

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Abstract

The theory for electron channelling patterns has been investigated. Calculations based on existing intensity expressions have been found inadequate for explaining recently observed deviations from Friedel's law. This is found to be the case even if the calculations are based on the full non-Hermitian eigenvalue matrix. The theory has hence been reinvestigated and a new intensity expression has been derived which includes the inter Bloch-wave coupling terms and is valid for non-centrosymmetric polyatomic crystals. The expression explains the observed asymmetries for GaSb which make it possible to determine unambiguously the correct non-centrosymmetric point group for this crystal. It is further found that the same effects in GaAs should be very weak in accordance with the non-observed deviation from Friedel's law in this case.

Introduction

Violation of Friedel's law in electron diffraction experiments is due to dynamical interactions between simultaneously excited Bragg beams (*e.g.* Kohra, 1954; Miyake & Uyeda, 1955; Fujimoto, 1959). Asymmetries which could be ascribed to this effect were reported for the non-centrosymmetric structure of ZnS by Thiessen & Molière (1939) and also by Miyake & Uyeda (1950). More recently, convergent-beam electron diffraction (CBED) and the bend extinction contour technique have proved to be well suited to reveal deviations from Friedel's law and consequently the absence of a centre of symmetry in a non-centrosymmetric structure (*e.g.* Goodman & Lehmpfuhl, 1968; Steeds, Tatlock & Hampson, 1973; Goodman, 1975; Steeds & Vincent, 1983).

In selected area channelling patterns (SACP), however, deviations from centrosymmetry have not been observed until recently. In a general investigation of the possible use of the SACP technique in structure studies (Høier & Marthinsen, 1986; Marthinsen, 1986; Marthinsen & Høier, 1988), effects have been observed for gallium antimonide which make it possible to determine the correct non-centrosymmetric point group in this case. Such effects, which may be ascribed to the failure of Friedel's law in electron channelling patterns, cannot be explained by any of the existing theoretical expressions as given, for example, by Reimer, Badde, Seidel & Bühring (1971), Spencer, Humphreys & Hirsch (1972), Yamamoto, Mori & Ishida (1978) or Spencer & Humphreys (1980).

The aim of the present work has been to investigate these observed effects more thoroughly. The theory is hence reinvestigated in order to obtain an expression which is able to account for the observations from gallium antimonide. As is well known from CBED, for example, the possible identification of a non-centrosymmetric structure is coupled to the interaction terms between the different Bloch waves. On this basis it may therefore be assumed that a many-beam intensity expression for channelling patterns has also to include these coupling terms. Their contribution to the channelling contrast from GaSb and GaAs is investigated in particular both theoretically and experimentally. Some preliminary results have been given previously (Marthinsen & Høier 1986*a*; Marthinsen, Anisdahl & Høier, 1987).

Experimental

The experiments were carried out in a JSM-840 scanning electron microscope. All the patterns reproduced below were obtained near a ⟨001⟩ zone.

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