be given, the $\frac{1}{2}\langle 111\rangle_c$ type appears preferable because the fit to observed structure factors is better, the bonding of the tetrahedra resembles the bonding in Fe_3O_4 and stresses can apparently be well relieved. The existence of free vacancies in $\frac{1}{2}\langle 100\rangle_c$ models is not favoured if vacancies are stabilized by the interstitials, but on the other hand, proposed diffusion mechanisms make use of free vacancies (Greenwood & Howe, 1972).

Through the present study a different lattice symmetry for the ordered superstructure and a lower point symmetry of the cluster than in previous investigations, are found.

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X-ray Diffraction and Transmission Electron Microscopy Study of Extremely Large-Period Polytypes in SiC

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Extremely large-period polytypes in SiC have been investigated by single-crystal X-ray diffraction and direct lattice imaging by electron microscopy, which has been found to be a more suitable technique for studying structures of extremely large periodicities. Some crystals giving rise to a diffuse streaking along $h0.l$ reciprocal lattice rows when studied by X-ray diffraction, showed the presence of extremely long-period polytypes when investigated by electron microscopy. The c periodicity of such SiC structures (having periodicities of more than 1000 Å) has been determined by this technique and the super-period block spacing is found to contain block spacings of $6H$, $15R$, $4H$ and $21R$ polytypes.

Introduction

A number of substances are known to crystallize in polytypic modifications and SiC is a prominent example of this category. The X-ray diffraction studies show that SiC crystals often possess one-dimensional disorder (Verma & Krishna, 1966). The occurrence of one-dimensional disorder in SiC crystals has been investigated in some detail by electron microscopy (Sato & Shinozaki, 1975), X-ray diffraction and chemical etching techniques (Ram, Dubey & Singh, 1974; Ram & Singh, 1976). The existence of one-dimensional disorder in SiC crystals is inferred from the continuous streaks usually found in single-crystal X-ray diffraction patterns along $h0.l$ reciprocal lattice rows. However it is shown that these streaks can also arise as a result of extremely high c periodicities of the crystals as their $h0.l$ spots cannot be resolved easily (Ram, Dubey & Singh, 1974). In some cases the structure of very large-period SiC crystals has been found to be composed of several units having a smaller repeat distance, *e.g.* a structure of extremely high *c* periodicity is built up of predominantly 147*R* structure units, the 147*R* structure is built up of predominantly 33*R* structure units and that of 33*R* is built up of structure units of 6*H* and 15*R* (Ram, Dubey & Singh, 1973). Similar structural patterns are obtained in the other SiC crystals as well. Our electron-microscopy results will further support these ideas.

By chemically etching out syntaxic structures, it is found that the coalesced structures are usually ordered and the interfaces between these ordered structures are sometimes not sharp and represent one-dimensionally disordered lamellae giving rise to continuous streaks superimposed over the discrete spots of the ordered structures (Ram & Singh, 1976).

It is of interest now to investigate the cause of such continuous streaks as they are normally attributed to one-dimensional disorder. This investigation has been undertaken both by X-ray diffraction and lattice imaging by electron microscopy. Any mechanism of polytype formation should be able to account for their common occurrence. It is pertinent to mention here that the occurrence of one-dimensional disorder does not fit in with the predictions of Frank's screw dislocation theory which otherwise is found to be a satisfactory mechanism of polytype formation in SiC.

1. X-ray diffraction studies of extremely high-period polytypes of SiC

The 10.*l* reflexions of a *c*-axis oscillation photograph of a SiC crystal are shown in Fig. 1(*a*). The line spots indicate the presence of a very high-period structure. Fig. 1(*b*) shows the 10.*l* row of the same crystal taken in a different region and range of oscillation. This pattern contains neatly resolved spots characteristic of the 98*H* polytype. It may be noted that the spot shape in this range of oscillation is not rectangular and that the fine-line spots observed in 1(*a*) are not resolved here. This means there is a very high-period structure which gives rise to closely spaced line spots in Fig. 1(*a*). The intensities of these reflexions are significant only in the vicinity of the spot positions corresponding to the 98*H* polytype. The line spots near 98*H* spot positions group together and appear as big rectangular spots. The rectangular spots on one side of the zero layer in Fig. 1(*a*) are distinctly separated because in between these spots the 98*H* reflexions are either extinguished or have very small intensities as is apparent from comparison with Fig. 1(*b*). The intensity sequence of reflexions on the other side of the zero layer line is different, giving rise to differences in spot intensities on the two sides in Fig. 1(*a*).

It is interesting to note that the rectangular spots in Fig. 1(*a*) correspond to the *c* periodicity of the 48*H* structure indicating that the 98*H* structure only gives rise to reflexions of significant intensity in the vicinity of the 48*H* spot positions.

Fig. 1(*c*) and (*d*) shows the 10.*l* row of the same crystal in different regions and ranges of oscillation. It may be seen that closely spaced line spots are resolved to some extent in Fig. 1(*c*) and are more clearly resolved in Fig. 1(*d*).

Fig. 2(*a*) shows the 10.*l* reflexions of another SiC crystal. It shows a heavy continuous streak connecting 10.*l* reflexions possibly indicating the presence of disorder. Two 10.*l* rows recorded in different regions and ranges of oscillation of the same crystal are illustrated in Fig. 2(*b*). It shows well resolved spots of the 66*H* polytype. It may be noted that there is no streak connecting the spots as is particularly clear from the central part of the row of spots. In regions where the spot intensities are strong, the spots appear to touch each other and give a false impression of streaking. This indicates that one has to be very careful; the continuous streaks in the present case do not imply the presence of a one-dimensional disorder.

Fig. 3 shows a final example of an X-ray pattern where streaking is observed along the 10.*l* row. Individual spots cannot be resolved any more. This might suggest that the crystal under examination has such a high periodicity that it gives rise to closely spaced line spots which merge and appear to form continuous streaks. This idea will be confirmed by the electron-microscope observations of the high periodicity. By only looking at the X-ray results one could have incorrectly called this a 'completely disordered polytype'.

2. Lattice imaging of long-period SiC polytypes in the electron microscope

2.1. *Introduction*

Direct lattice resolution in transmission electron microscopy has become a powerful tool in the study of mixed-layer compounds (Van Landuyt, Amelinckx, Kohn & Eckart, 1974), (Anderson & Hutchison, 1975) and long-period complex oxides (Cowley & Iijima, 1972; Allpress & Sanders, 1973). For structures with very large repeat distances which can only be studied with considerable difficulties by X-ray methods, supplementary information can be provided by lattice imaging in the electron microscope. Also, for studying irregular stacking sequences or disorder in the stacking of the layers, lattice resolution can be useful.

For long-period stacking sequences associated with the mechanism of growth, such as in SiC, this technique can be used for complementing X-ray results. It can be shown that under suitable circumstances it is possible to establish a one-to-one correspondence between image contrast and structural features.

In a chemically simple compound such as SiC where all (0001) layers have the same composition, long-period polytypes are formed owing to periodic changes in the stacking sequence of the close-packed layers.

The detailed formation mechanism of those polytypes is still an open question but a quite generally accepted possibility is that a screw dislocation having a very large Burgers vector would be active and would repeat an irregular stacking sequence at regular intervals. These intervals can be very large, even more than 1000 Å (Verma & Krishna, 1966).

Such one-dimensional long-period structures give rise to diffraction patterns consisting of rows of very closely spaced reflexions. This is so for X-ray patterns (*e.g.* Fig. 4) as well as for electron diffraction patterns (*e.g.* Fig. 8). Both diffraction patterns are difficult to analyse and therefore lattice imaging is used to establish the stacking sequence. $00.l$ reflexions cannot be used for this purpose since for a nH or nR polytype they are all structurally forbidden except those with $l=n,2n,3n,\ldots$. Other reflexions in the $00.l$ row which are present on most patterns only appear by double diffraction. For dark-field lattice imaging reflexions of the type $10.l$ were used.

2.2. *Experimental details*

The high-period structures of SiC are often found in syntaxic coalescence with other polytypic structures and it becomes difficult to get even minute pieces of a crystal which are exclusively a high-period structure. From such minute pieces of crystals which were used for X-ray examination, samples suitable for electron microscopic examination were prepared by crushing the pieces into powder form and dispersing the powdered fragments on carbon grids.

The most common cleavage plane in SiC is (0001) giving rise to specimens in the basal orientation. However cleavages parallel to prismatic planes $\{11\bar{2}0\}$ are also obtained and thin samples produced as a result of such cleavages are found suitable for the lattice resolution studies. The samples were examined in a 100 kV electron microscope equipped with a double-tilt specimen holder. Using the goniometer stage specimens are brought into an orientation such that the incident electron beam is exactly parallel to the c planes and moreover that a row of $10.l$ reflexions is active. This can be achieved by using the electron microscope in diffraction mode and tilting alternately along both axes of the double-tilt specimen holder. In most cases a whole reciprocal prismatic plane was equally excited. Dark-field images were made by selecting in the objective aperture a basic $10.l$ reflexion together with a number of diffraction spots belonging to the long-period polytype. The dark-field micrographs were made by beam deflexion without changing the crystal orientation.

Owing to experimental difficulties in preparing samples suited for electron microscopy from crystals of 0·05 mm diameter not all material investigated by X-rays could be examined by electron microscopy. Moreover since probably an infinite number of polytypes exist in SiC we will only discuss a limited number of examples.

2.3. *Experimental results*

(*a*) 6*H* and 15*R*. Most of the complicated SiC polytypes are built up of units having a 6*H* or 15*R* structure. Fig. 4(*a*) and (*b*) shows the lattice images of both polytypes together with their respective diffraction patterns. For the 6*H* phase the lattice fringes are separated by 15·1 Å while for 15*R* the observed interplanar spacing amounts to 12·6 Å. In both examples the stacking is not completely perfect; a stacking fault can be recognized.

(*b*) 126*R*. This polytype was particularly chosen for the present study since this type of structure is difficult to work out. The $10.l$ row of spots of a single-crystal X-ray diffraction oscillation photograph of the 126*R* polytype is shown in Fig. 5(*a*). The pattern indicates that it is a perfectly ordered structure having $c=316{\cdot}76$ Å and the intensity distribution of the spots indicates that the structure of 126*R* is not dominantly built up of any one of the common structures 6*H*, 15*R* or 21*R*. The electron diffraction pattern of part of this crystal is shown in Fig. 5(*b*). The periodicity deduced from the lattice-imaging micrograph (Fig. 5*c*) corresponds to one third of the c-repeat period of the 126*R* polytype, *i.e.* 105·6 Å. This periodicity is subdivided into different blocks of approximately 20 Å (eight layers), 17·6 Å (seven layers) or 12·6 Å (five layers) in the way represented in Fig. 6. The stacking within the crystal is surprisingly perfect and no faults could be detected in the periodic stacking of the 42-layer structure.

On the basis of the majority of the structures worked out for SiC, the blocks of seven-layer thickness are most likely to be 34 and those of five-layer thickness to be 32 in Zhdanov notation. Thus different combinations of the first eight layers followed by the stacking sequence of 15*R* and 21*R* as depicted above are expected to give rise to the 126*R* structure.

Similar examples of such perfect long-period polytypes have been studied by Yessik, Shinozaki & Sato (1975) mainly by electron diffraction.

(*c*) *Extremely large-period polytypes.* In some cases single crystals with a very large repeat unit along the c axis can be formed. On the X-ray diffraction pattern recorded from such crystals closely spaced spots superimposed on a continuous background can be detected along the $h0.l$ rows (Fig. 3). The electron diffraction pattern of such a crystal is as confusing as the X-ray pattern and the same characteristics are observed: very dense spots superimposed on a continuous streaking along the $h0.l$ rows (Fig. 7). Both techniques fail to solve the exact structure of the polytype. With lattice resolution it immediately becomes clear that the crystal is not completely disordered but that a super-

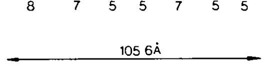
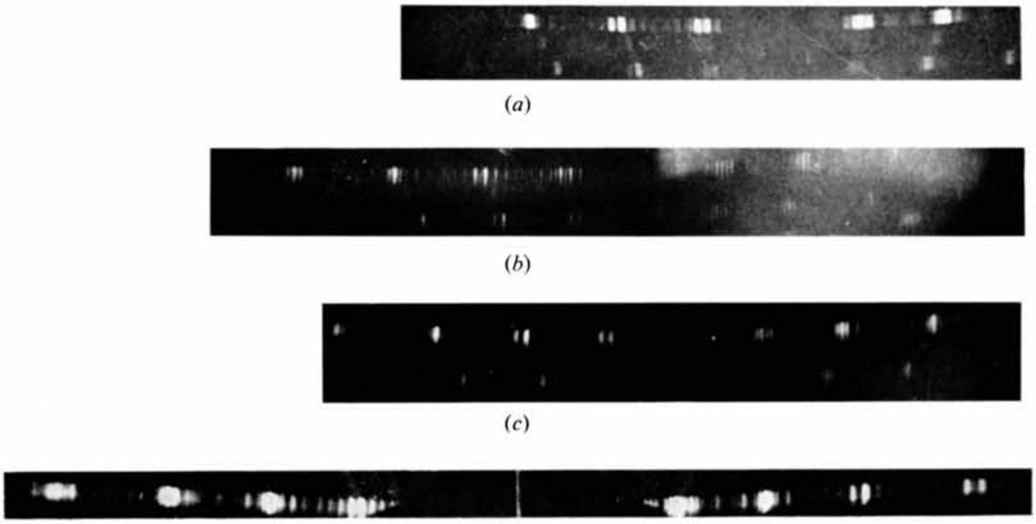


Fig. 6. Schematic representation of the stacking sequence of the 126*R* polytype.

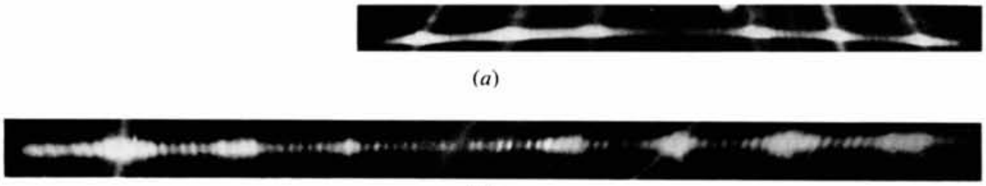

(*a*)

(*b*)

(*c*)

(*d*)

Fig. 1. (*a*)–(*d*) The 10.*l* row of spots of 98*H* single crystal recorded on 15° *c*-axis oscillation photographs taken with Cu *K* radiation with a camera of radius 3 cm (all × 3·5).


(*a*)

(*b*)

Fig. 2. The 10.*l* row of spots of a 66*H* crystal recorded on 15° *c*-axis oscillation photographs with Cu *K* radiation with a camera of radius 3 cm. (*a*) × 3·5, (*b*) × 4·9.


(*d*)

Fig. 3. The 10.*l* row of spots of a disordered polytype recorded on 15° *c*-axis oscillation photograph with Cu *K* radiation and camera of radius 3 cm (× 4·9).

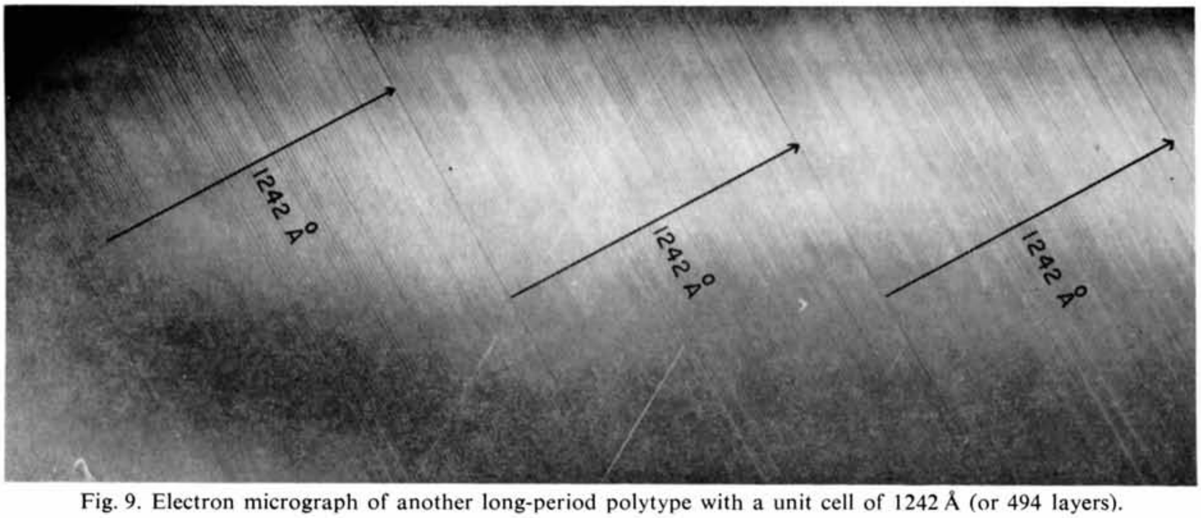


Fig. 9. Electron micrograph of another long-period polytype with a unit cell of 1242 Å (or 494 layers).

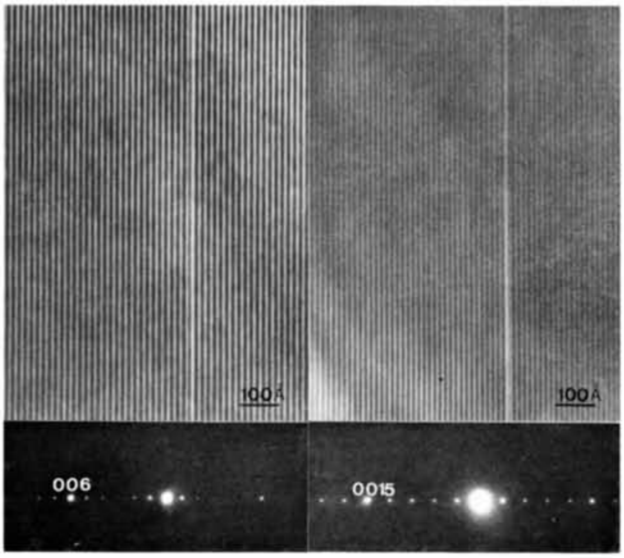
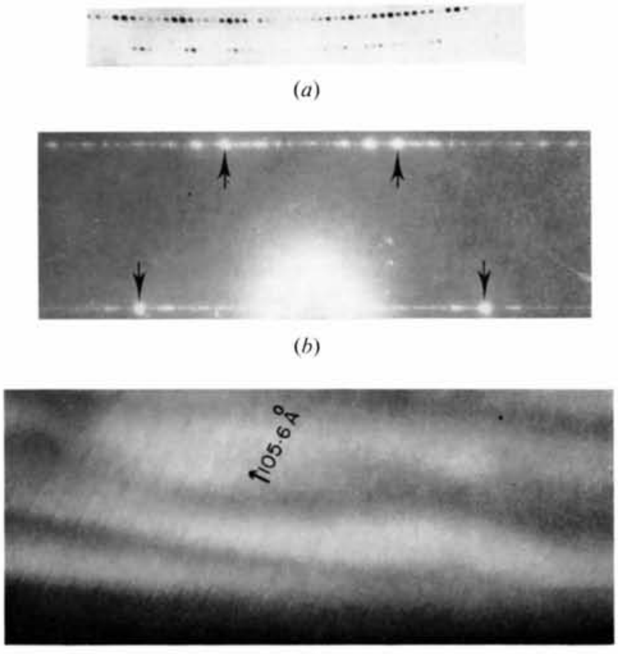


Fig. 4. Lattice images of (*a*) a 6*H* and (*b*) a 15*R* polytype in SiC. The corresponding diffraction patterns are shown as an inset. The stacking faults in both polytypes are easily recognized (Courtesy of J. Van Landuyt and S. Amelinckx).



(*a*)

(*b*)

(*c*)

Fig. 5. (*a*) A 15° *c*-axis oscillation photograph with Cu *K* radiation of the 126*R* polytype, (*b*) Electron diffraction pattern of the same 126*R* polytype. Arrows indicate basic reflexions, (*c*) Direct lattice imaging of 126*R* SiC; a periodicity of 105·6 Å is observed.

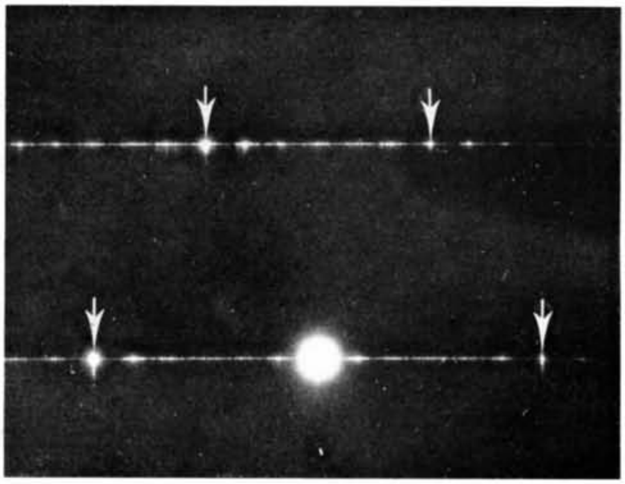
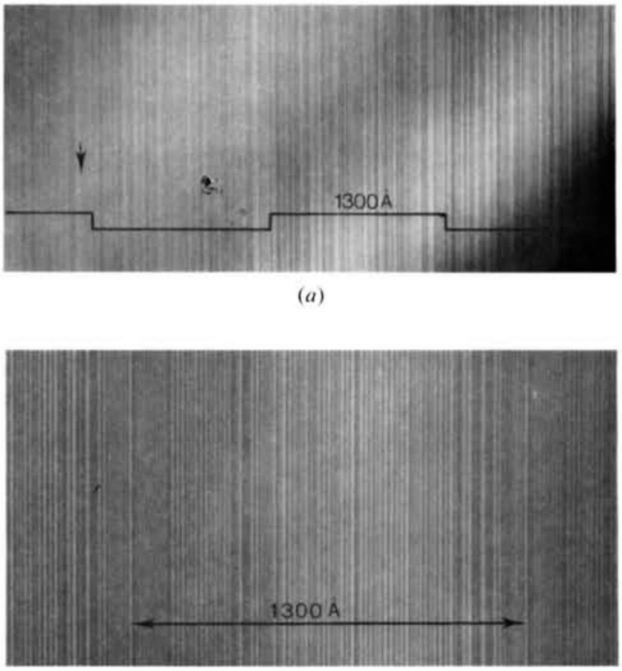


Fig. 7. Electron diffraction pattern of a long-period polytype in SiC. The direct lattice image of the crystal giving rise to this pattern is shown in Fig. 8. Arrows indicate the basic reflexions.



(*a*)

(*b*)

Fig. 8. (*a*) Lattice resolution of the long-period polytype of SiC mentioned in Fig. 7. The repeat distance amounts to 1300 Å. A stacking fault is indicated. (*b*) Enlargement of the supercell.

periodicity of about 1300 Å is present (Fig. 8*a*). The 1300 Å unit is shown enlarged in Fig. 8(*b*). This superblock itself consists of an irregular sequence of smaller units giving rise to lattice spacings of 10, 12·6, 15·1 and 17·6 Å corresponding to the 4*H*, 15*R*, 6*H* and 21*R* polytypes respectively. Another example shown in Fig. 9, having a 1242 Å periodicity (corresponding to 494 close-packed layers) is found to consist of 37 spacings of 6*H*, 32 of 15*R*, 10 of 21*R* and 8 of 4*H*. The frequency of occurrence of the polytypes constituting the super-blocks is such that $6H > 15R > 21R > 4H$. Within such long-period supercells it is easy of course to introduce stacking faults or even to break down the periodicity over a limited distance. The presence of such faults will cause a supplementary streaking on the diffraction pattern. If more faults are present the streaking will become more pronounced and this will affect the intensities especially for X-ray diffraction where an average is taken over a larger area. Such a fault is indicated in Fig. 8(*a*). If too many faults occur, the periodicity is lost and we have a completely long-range disordered crystal. During the present investigation using the lattice-imaging technique, crystals were found to be completely disordered over ranges of more than 5000 Å, *i.e.* no smaller repeat unit could be detected.

3. Conclusion

X-ray diffraction studies of single crystals of SiC have shown that the presence of diffuse streaks along $h0.l$ rows cannot necessarily be attributed to *complete* disorder. Careful analysis sometimes reveals discrete spots, suggesting the presence of long-period polytypes. When the periodicity becomes too large conventional X-ray diffraction becomes very difficult and therefore the lattice-imaging technique by electron microscopy has been applied to determine the stacking of such extremely large polytypes. The different polytypes having periodicities of more than 1000 Å are built up of units of the 6*H*, 15*R*, 4*H* and 21*R* polytypes of SiC.

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Spin Point Groups

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The 598 classes of nontrivial spin point groups are derived and tabulated. The relationship between classes of nontrivial spin point groups and the 32 classes of trivial magnetic point groups and the 58 classes of nontrivial magnetic point groups is also given.

1. Introduction

The theory of *spin groups*, generalized magnetic groups defined to describe the symmetry of spin arrangements in crystals, has been given by Litvin & Opechowski (1974). The theory of spin groups has been applied in the analysis of neutron diffraction data to determine spin arrangements in crystals. The so-called *nontrivial spin translation groups* and the possible magnetic reflexions of unpolarized neutrons elastically scattered