Lattice-Imaging Studies on Intergrowth Structures of Silicon Carbide

By S. R. Singh and G. Singh

Department of Physics, Banaras Hindu University, Varanasi-221 005, India

Abstract

Bright-field lattice images of three syntactically coalesced polytypes of SiC were taken with a view to deriving structural information. A high-period structure $400H$ is found to consist of seven unit cells of $150R$ and one unit cell of $150R_A$. The $150R$ structure is built up of ten $15R$ unit cells; consecutive $15R$ subunits in obverse and reverse orientation give rise to sudden changes in contrast in the image. Complete structure determination of $150R$ and $150R_A$ is thus possible. The structures were confirmed by comparing the calculated and observed X-ray intensities. An imaging code was established which helped in the structure determination of the $400H$ polytype.

Introduction

It is a well known fact that silicon carbide crystallizes in various ordered structures, each of which is characterized by a unique one-dimensional stacking sequence of Si–C double layers. The c repeat period of these structures depends on the number of Si–C double layers in the unit cell and lies in a wide range from 1 nm to more than 100 nm. It becomes quite cumbersome to work out and describe polytype structures of particularly high periodicities in terms of stackings of individual Si–C double layers. However, it is usually found that large-period unit cells consist of regular stackings of unit cells of more common structure types like $6H$, $15R$ and $4H$ which are periodically interrupted by stacking faults, thereby generating structures of large c periodicities. Therefore, it has become a common practice to describe any large-period structure in terms of the stackings of smaller unit cells followed by sequences of some faulted layers. The problem of working out polytype structures becomes too complicated when a high-period unit cell is built up of a mixture of different common polytype unit cells [*e.g.* $126R$ polytype with $(53\ 43\ 32\ 23\ 33\ 33\ 23)_3$ structure in Zhdanov notation (Dubey & Singh, 1978)] or of unit cells of the same periodicity but frequently occurring in microtwin orientation. It is in such cases that lattice imaging has been found to be very useful and the present paper is concerned with the structure determin-

ation of such polytypes, $150R$, $150R_A$ and $400H$, with the help of lattice imaging.

It has been recognized that lattice imaging in the electron microscope is a powerful tool for studying local structural variations in crystals, which is not possible by X-ray diffraction (Allpress & Sanders, 1973; McConnell, Hutchison & Anderson, 1974; Buseck & Iijima, 1974, 1975) owing to its averaging effect. The different stacking modes of constituent blocks or layers of particularly large-period structures have been made directly visible in a number of mixed-layer compounds, minerals and complex oxides by this technique (Van Landuyt, Amelinckx, Kohn & Eckart, 1973, 1974; Cowley & Iijima, 1972; Allpress & Sanders, 1973; Buseck & Iijima, 1974). However, the direct correlation of the image contrast with the crystal structure is possible only under very stringent experimental conditions (Allpress & Sanders, 1973) and instances of complete structure determination from lattice images have been very limited. The present communication reports the result of one such effort making use of one-dimensional lattice images of SiC.

Experimental details

During our systematic investigations on one-dimensional disorder in SiC crystals we have been selecting crystals showing continuous streaks along $h0.l$ reciprocal-lattice rows in X-ray diffraction and then examining them by the lattice-imaging technique.

One of these crystals was a thin platelet with well developed basal faces. One corner of this platelet when examined by a c-axis oscillation photograph (Fig. 1a) showed spots of some intergrown polytypes. This part of the crystal was broken into several pieces and the $10.l$ row from one of these is shown in Fig. 1(b). From Fig. 1(b) the following are observed. (1) The crystal piece contains two polytypes in parallel intergrowth. Both the polytypes are rhombohedral with the same periodicity ($c = 12.5$ nm) but in obverse and reverse orientation. The crystal piece consists predominantly of one of these structures (hereafter called $150R$) with only a small trace of the other in reverse orientation (to be termed subsequently as $150R_A$) which is confined to only a small part of the crystal. This is indicated by the

feeble intensities of its reflections and the difference in spot sizes of the two structures. (2) The structure of $150R$ seems to be somewhat based on $15R$ because its spots corresponding to $15R$ spot positions are comparatively strong and its spots between any two consecutive $15R$ spot positions have a very similar intensity sequence. (3) The spots show some unusual structural extinctions because $10.l$ reflections are extinguished when $l = 30n - 5$ (where $n = 0, \pm1, \pm2, ...$) unlike other SiC polytype structures where $10.l$ reflections are absent only when $l = \pm n, \pm 2n, ...$ for a nH or nR polytype. (4) Based on usual methods (Verma & Krishna, 1966) of structure determination of SiC polytypes, a large number of probable structures based on $15R$ were tried without success. (5) The $150R$ spots split up into many finer spots indicating the presence of a superperiodicity based on $150R$ (Ram, Dubey & Singh, 1973; Dubey, Ram & Singh, 1973). The splitting may be noted only in large-l reflections because interlayer separation increases with increasing ζ value in oscillation photographs. In view of these characteristics it was realized that the structure of $150R$ is of unusual type and lattice-imaging studies may give useful information in its structure determination.

Under kinematical conditions, $00.l$ reflections in any nH or nR polytype of SiC are structurally extinguished except when $l = \pm (n, 2n, 3n, ...)$. This means that the $00.l$ reciprocal-lattice row is identical for all the polytypes. Consequently, lattice fringes formed by kinematically allowed $00.l$ reflections alone for any polytype will give identical fringes of 0.25 nm periodicity, which represents the interlayer separation between consecutive Si or C layers. The presence of kinematically absent reflections in the $00.l$ row in electron diffraction is mainly due to multiple diffraction. Any distinction between bright-field lattice images of different polytypes is therefore possible only because of multiply diffracted beams occurring at kinematically absent $00.l$ positions.

The crystal piece examined by X-rays was crushed in an agate mortar and fine powder fragments were dispersed on a holey carbon grid for examination in a Philips EM300 electron microscope equipped with a high-resolution double-tilt goniometer stage. For deriving any structural information the most desirable condition is to take a bright-field lattice image by including symmetrical reflections. Therefore, a suitable crystal flake was oriented so as to excite the $h0.l$ reciprocal-lattice net over the whole range and bright-field lattice images were obtained using an objective aperture of diameter 3.3 nm^{-1}, which in the case of $150R$ allows only forty systematic reflections of $00.l$ type. Fig. $2(a)$ shows a bright-field lattice image formed by kinematically absent $00.l$ reflections ($l \leq \pm 60$) and the corresponding diffraction pattern depicting the objective aperture position is shown in Fig. $2(b)$.
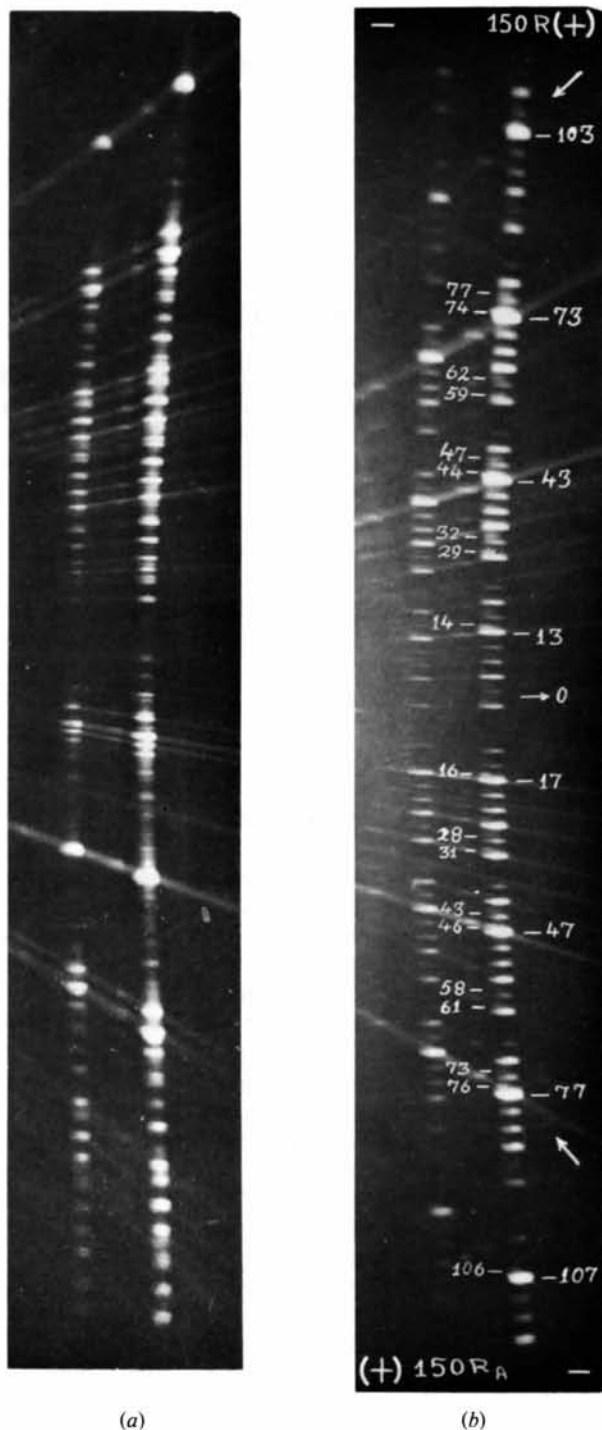

Fig. 1. (a) The $10.l$ row of reflections as recorded on a $15°$, c-axis oscillation photograph of the parent SiC crystal. (b) The $10.l$ row of reflections from a tiny piece of the parent crystal. The prominent horizontal spots correspond to $150R$ while faint spots of smaller size correspond to $150R_A$. The reflections of the two structures are marked. Fine structure in $150R$ reflections, particularly at large l values, may be noted.

Structure determination of 150R

The lattice imaging of a number of extremely high-period polytypes including that of 126R of SiC was reported recently (Dubey, Singh & Van Tendeloo, 1977). Subsequently it was shown (Dubey & Singh, 1978) that the lattice image of 126R is capable of revealing stackings of constituent unit cells of common polytypes (*viz* 6H, 15R and 21R) forming the 126R repeat period. This was confirmed by comparing the calculated and observed X-ray intensities. Yessik, Shinozaki & Sato (1975) have also attempted to determine the stacking sequence of smaller structure units constituting some large period structures but these structures have not been confirmed by X-ray methods.

A closer look at the bright-field lattice image (Fig. 2a) reveals the following. (a) The entire image consists of fringes of periodicity 1·25 nm of which some are in dark contrast while others are in bright contrast. These fringes correspond to the **c**/3 periodicity of the 15R polytype and are due to conspicuously strong reflections at 15R spot positions (Fig. 2b). (b) The sequence of fringes in bright and dark contrast shows another periodicity of 12·5 nm, which consists of ten 1·25 nm fringes as shown in Fig. 2(a). The 12·5 nm wide blocks correspond to consecutive reflections in the 00.*l* row and therefore represent the **c**/3 periodicity of the 150R polytype. (c) Every eighth block of 12·5 nm periodicity is faulted, which is distinguished by a different sequence of 1·25 nm fringes in bright and dark contrast. These are marked 150R_A in Fig. 2(a). Occurrence of these faulted blocks at regular intervals reveals a still higher periodicity of 100·7 nm (marked by 400H in Fig. 2a), which corresponds to the high periodicity inferred from the fine structure of the X-ray reflections as mentioned before.
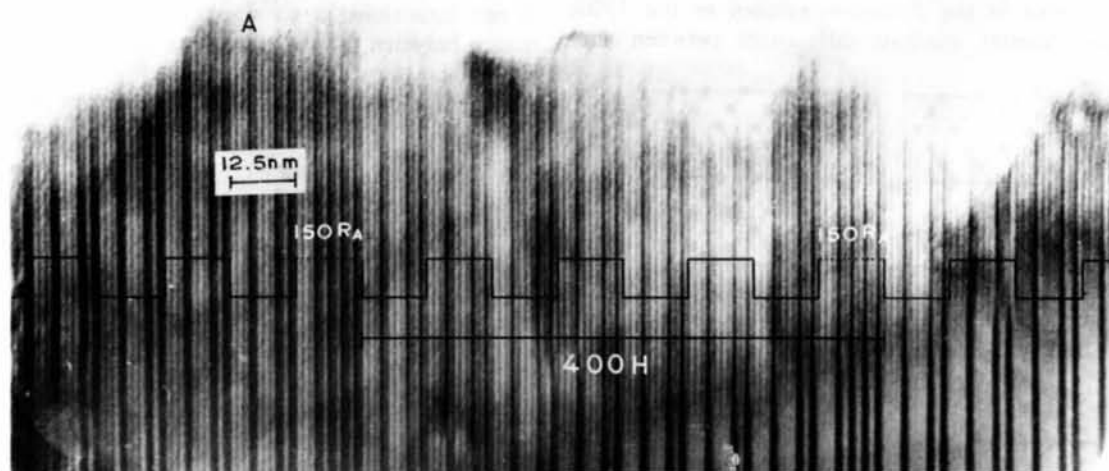
(a)
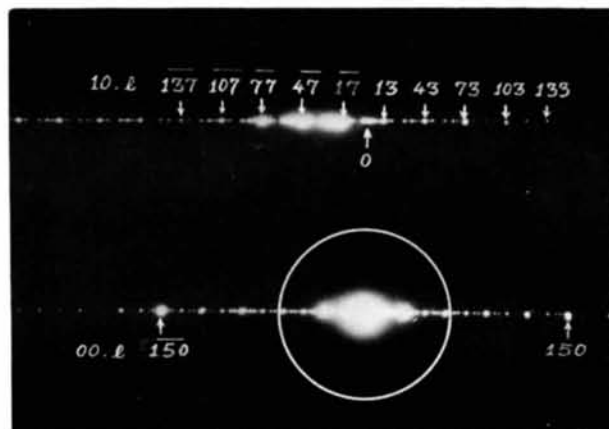
(b)

Fig. 2. (a) A bright-field lattice image taken with 40 symmetrical 00.*l* reflections revealing fringes of 1·25 nm periodicity corresponding to 15R. The 15R unit cells in obverse & reverse orientations are revealed by marked changes in contrast. A superperiod of 100·7 nm occurs due to periodic intergrowth of 150R_A in 150R matrix. Sudden changes in contrast are more apparent in the region marked A. (b) Electron diffraction pattern showing to h0.*l* reciprocal-lattice net. The beams included in the objective aperture are encircled.

The X-ray intensities of the 150R polytype show that its structure is predominantly built up by stackings of 15R unit cells, as is also confirmed from the lattice image where each 150R block contains ten 15R periodicities. This can be so only when all the ten 15R unit cells are not identically stacked in a 150R structure. This is indeed revealed in the lattice image where three of the ten 15R fringes are conspicuously in dark contrast compared to the rest. One distinct possibility of alternative stackings of 15R unit cells may be that some of them are in obverse orientation while others are in reverse orientation. They are represented by 32 and 23 in Zhdanov notation. Two consecutive unit cells of 15R with 32 and 23 structures acquire nearly twinned orientation as seen from the zig-zag sequence of Si or C atoms in the (11.0) plane in Fig. 3. Keeping this in view, we realized that the sudden change in contrast in adjacent 15R fringes in the lattice image may arise from obverse and reverse orientation of 15R unit cells and therefore correspond to 32 and 23 or *vice versa* in the Zhdanov symbol of the 150R structure. Similar contrast differences between suc-

cessive twinned bands have also been observed in ferrite structures (Van Landuyt, Amelinckx, Kohn & Eckart, 1973). Treating 15R fringes in dark contrast as 32 and 23 and those in bright contrast as 23 and 32 respectively we arrive at two structures of 150 R as read from the lattice image.

(i) $[(23)_3 32 (23)_3 32 23 32]_3$,

(ii) $[(32)_3 23 (32)_3 23 32 23]_3$.

These two represent the same structure in obverse and reverse orientation and therefore are indistinguishable in X-ray diffraction.

Ramsdell (1944) and Verma & Krishna (1966) have shown that it is sufficient to compare the calculated and observed intensities of 10.l reflections alone to determine the correctness of a proposed structure for any SiC polytype. Accordingly, the intensities of 10.l reflections were calculated for the above structure and corrected for Lorentz and polarization factors. The match between the calculated and visually observed X-ray intensities is so good that even a qualitative match between the two as shown in Table 1 is deemed
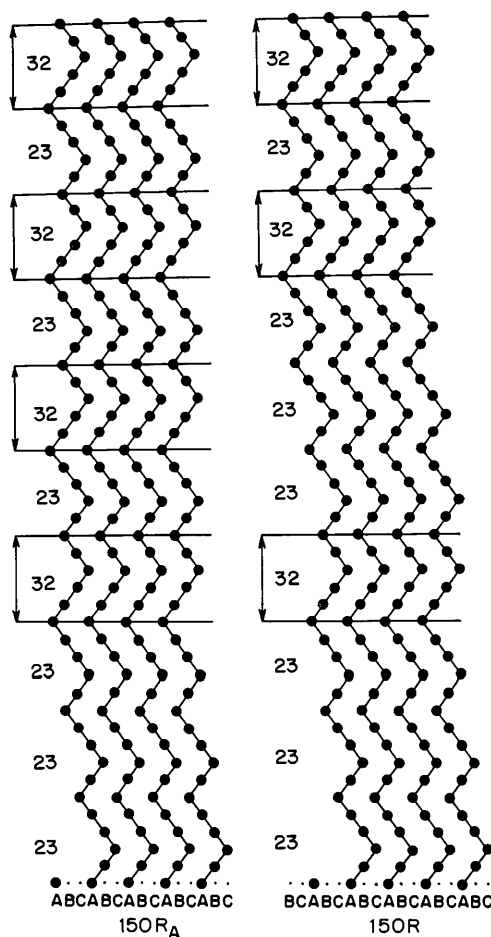

Fig. 3. The zig-zag sequence of Si or C atoms in the (11.0) plane. 15R fringes which appear in dark contrast in Fig. 2(a) are marked.

Table 1. *Calculated and observed relative intensities for the structure* 150R

l in 10.l	Calculated intensities	Observed intensities*	l in 10.l	Calculated intensities	Observed intensities*
1	0·59	vw	2	3·6	ms
4	5·9	s	5	0	a
7	1·8	ms	8	0·17	vvw
10	1·1	w < 10.7	11	1·7	w > 10.10
13	19·1	s > 10.4	14	0·7	vw > 10.1
16	0·97	w < 10.10	17	38·1	vs > 10.34
19	5·3	s < 10.4	20	4·1	s < 10.4̲
22	0·7	vw	23	7·8	s > 10.2̲0̲
25	0	a	26	25·9	vs < 10.1̲7̲
28	16·4	s < 10.13	29	2·8	ms > 10.1̲1̲
31	2·9	ms > 10.7	32	19·7	s > 10.13
34	34·3	vs	35	0	a
37	14·2	s < 10.28	38	1·4	w < 10.1̲1̲
40	10·0	s < 10.37	41	15·0	s < 10.3̲2̲
43	131·8	vvs	44	3·8	s < 10.5̲0̲
46	3·2	ms ≃ 10.31	47	94·3	vvs
49	8·0	s < 10.40	50	4·8	s > 10.2̲0̲
52	0·57	vw ≃ 10.1	53	5·3	s > 10.5̲0̲
55	0	a	56	13·4	s < 10.4̲1̲
58	8·2	s ≃ 10.49	59	1·3	w ≃ 10.3̲8̲
61	1·5	w < 10.7	62	10·2	s < 10.5̲6̲
64	20·4	vs < 10.34	65	0	a
67	9·4	s > 10.70	68	1·0	w < 10.3̲8̲
70	8·0	s	71	12·6	s < 10.5̲6̲
73	124·8	vvs ≃ 10.43	74	3·8	s ≃ 10.4̲4̲
76	3·6	ms ≃ 10.46	77	110·7	vvs
79	9·8	s ≃ 10.67	80	5·8	s ≃ 10.5̲3̲
82	0·66	vw	83	5·7	s ≃ 10.8̲0̲
85	0	a	86	10·4	s > 10.6̲2̲
88	4·7	ms > 10.76	89	0·8	vw
91	0·54	vw	92	3·1	ms
94	4·6	ms ≃ 10.88	95	0	a
97	1·6	w	98	0·17	vvw
100	1·3	w	101	2·2	ms
103	24·6	vs	104	0·82	vw
106	0·93	w	107	31·33	vs
109	3·4	ms	110	2·3	ms

* vvs, vs, s, ms, w, vw, vvw and a stand for very very strong, very strong, strong, medium strong, weak, very weak, very very weak and absent respectively.

sufficient proof for the correctness of the determined structure.

The atomic parameters derived from $[(23)_3 32(23)_3 32\ 23\ 32]_3$ are: 50 Si atoms at $0,0,tz$, where $z = 1/150$ and $t = 0, 4, 6, 8, 12, 15, 18, 22, 25,$ 29, 31, 33, 37, 39, 41, 43, 47, 49, 51, 53, 57, 60, 64, 66, 70, 74, 76, 78, 82, 85, 88, 92, 95, 98, 102, 105, 109, 111, 113, 117, 119, 121, 123, 127, 130, 134, 136, 140, 144, 146; 50 Si atoms at $\frac{2}{3}, \frac{1}{3}, tz + \frac{1}{3}$; 50 Si atoms at $\frac{1}{3}, \frac{2}{3}$, $tz + \frac{2}{3}$; 150 C atoms above each Si atom at a distance $p = 1/200$ having coordinates $0,0,p$ plus the co-ordinates of 150 Si atoms.

The structure determination of $150R_A$

From the lattice image (Fig. 2a) it is observed that every eighth block of $150R$ is faulted in the sense that the sequence of fringes in dark and white contrast are different both in number and position compared to other blocks. Treating these fringes in the same way as in other $150R$ blocks, these faulted blocks represent an alternative $150R$ structure, viz $[(23)_3 32\ 23\ 32\ 23\ 32\ 23\ 32]_3$. This structure will hereafter be termed $150R_A$. Representing the number of Si—C double layers in $\triangle$ orientation by n_+ and that in $\triangledown$ orientation by n_-, the $150R_A$ structure has $n_+ - n_- = -1$ whereas that for $150R$ is $+1$. Therefore, $150R$ and $150R_A$ structures are mutually in obverse and reverse orientations (Verma & Krishna, 1966). Since the X-ray diffraction pattern of the composite crystal (Fig. 1b) also showed the presence of two $150R$ structures in obverse and reverse orientation, it was conjectured that these structures correspond to $150R$ and $150R_A$.

Polytype structures in SiC are often coalesced and they grow under almost identical thermodynamic conditions. When two or more polytype structures grow in syntactic coalescence the transition from one structure to the other may not be abrupt. Rather, it is likely that the boundary region between two inter-grown structures may contain unit cells of both the structures which may sometimes stack in a particular fashion and give rise to a superperiod based on both the coalesced structures. In fact it appears that the crystal flake whose lattice image is shown in Fig. 2(a) is from the boundary region between two coalesced structures, viz $150R$ and $150R_A$.

The X-ray intensities of $10.l$ reflections of the $150R_A$ were calculated for the structure $[(23)_3 32\ 23\ 32\ 23\ 32\ 23\ 32]_3$ which was inferred from the lattice image and matched with the observed X-ray intensities of Fig. 1(b). The calculated intensities match well with the observed intensities of all the observable $10.l$ reflections of $150R_A$ (Fig. 1b) and therefore the above structure is the correct structure.

Atomic parameters derived from $[(23)_3 32\ 23\ 32\ 23\ 32\ 23\ 32]_3$ are: 50 Si atoms at $0,0,tz$, where $z = 1/150$ and $t = 0, 4, 6, 8, 12, 15, 18,$

22, 25, 28, 32, 35, 38, 42, 45, 48, 52, 55, 59, 61, 63, 67, 69, 71, 73, 77, 79, 81, 83, 87, 89, 91, 93, 97, 99, 101, 103, 107, 110, 114, 116, 120, 124, 126, 130, 134, 136, 140, 144, 146; 50 Si atoms at $\frac{2}{3}, \frac{1}{3}, tz + \frac{1}{3}$; 50 Si atoms at $\frac{1}{3}, \frac{2}{3}, tz + \frac{2}{3}$; 150 C atoms above each Si atom at a distance $p = 1/200$ having coordinates $0,0,p$ plus the coordinates of 150 Si atoms.

The structure of $400H$

As mentioned before, the lattice image (Fig. 2a) shows the regular occurrence of one block of $150R_A$ after every seven blocks of $150R$, thereby giving rise to a superperiod of 100.7 nm. There are only three repeat periods of this superperiod in the lattice image which may or may not represent a periodicity in the long range. However, the superperiodicity inferred from the fine structure of X-ray spots (Fig. 1b) corresponds to the same periodicity as observed in the lattice image. Therefore it is reasonable to believe that the three units of 100.7 nm periodicity are a part of the high-period structure. In a similar context, in the case of enstatite, Buseck & Iijima (1975) prefer to call a pattern periodic if it is repeated at least thrice in the lattice image.

Using the same imaging code for fringes in black and white contrast as in the case of $150R$ and $150R_A$ one can reliably arrive at the following structure of the superperiod:

$$[\{(23)_3 32(23)_3 32\ 23\ 32\}_7$$
$$\{(23)_3 32\ 23\ 32\ 23\ 32\ 23\ 32\}].$$

The above structure has $n_+ - n_- = -30$ which shows that it is a hexagonal structure (Verma & Krishna, 1966). Since the superperiod is found to contain 400 double layers of Si and C, it is identified as $400H$. Normally it becomes very difficult to distinguish between hexagonal and rhombohedral polytypes when the c periodicity becomes quite large because of the closeness of X-ray reflections about the zero layer line. Therefore, lattice imaging is found to be a suitable technique for identifying extremely large periodicities in SiC polytypes by establishing a genuine imaging code. This is the longest-period polytype whose structure has been determined.

Discussion

Previously it was believed that most of the large-period polytypes of SiC are based on either of the commonly occurring structures, viz $6H$, $15R$ and $4H$. However, recently it has been found (Ram, Dubey & Singh, 1973; Dubey, Ram & Singh, 1973) that the building blocks of these large-period polytypes were not confined to these three common structures, but other structures such as $21R$, $33R$, $147R$, $189R$, etc. also constitute the building blocks of large-period structures.

These conclusions arrived at mainly by X-ray diffraction studies are elegantly corroborated by a similar case of the 150R crystal, whose lattice image (Fig. 2a) confirms the X-ray diffraction observations to this effect. In the present case X-ray diffraction reveals a superperiod based on 150R, which in turn is based on the 15R structure. The lattice image not only confirms these observations but also helps in identifying the superperiod.

For establishing a correlation between the image contrast and the structure the most desirable condition is to take a bright-field image including symmetrical reflections from extremely thin samples which may behave as phase gratings. However, the present example shows that in polytypic structures of high periodicity, sufficient structural information may be derived from the spatial frequencies in a one-dimensional image even when kinematically absent reflections are involved in the image formation. This means that the correlation of the lattice image with structure in terms of periodicities and stackings of the constituent unit cells does not need as stringent conditions as are needed for correlating the projected charge density with the image. It has been shown (Dubey & Singh, 1978) in the case of the 126R SiC polytype that similar information is available even from dark-field lattice images (including 10.l reflections only in the objective aperture), which helped in narrowing down the most probable structures to 29 and thus led to the complete structure determination. However, from the bright-field image in the present case it has been possible to arrive at the correct structure almost immediately. Jepps, Smith & Page (1979) have recently shown, by taking a high-resolution tilted-beam image (beam tilted to a position between 10.0 and 00.0 so that 10.2 and 10.$\bar{2}$ beams are included in the aperture), that it is possible to image the stacking sequence of Si–C double layers in the (11.0) plane, thereby directly reading the Zhdanov symbol of the structure. The present study shows that useful structural information in long-period structures can be derived with microscopes with only moderate resolution.

Conclusion

Lattice-imaging studies on high-period SiC polytypes reveal nicely the stackings of the constituent smaller unit cells, and rhombohedral subunits in obverse and reverse orientations show up clearly in the form of sudden changes in contrast. This enables the determination of even unusually complex structures, which is otherwise very difficult by usual X-ray diffraction methods. With the help of lattice imaging, the superperiod of 100·7 nm is clearly seen to consist of large-period structures like 150R, which is only faintly detectable from X-ray diffraction patterns. Lastly, it is possible to derive structural information on SiC polytypes at the unit-cell level of common polytypes like 6H, 15R and 4H even when kinematically absent reflections are used to obtain the bright-field image. This example along with our previous (Dubey & Singh, 1978) derivation of structural information on 126R from a dark-field lattice image shows that lattice imaging even at moderate resolution is a powerful supplementary tool for structure determination in SiC polytypes, particularly in the unusually complex structures which are very difficult to work out with X-ray diffraction methods alone.

References

ALLPRESS, J. G. & SANDERS, J. V. (1973). *J. Appl. Cryst.* **6**, 165–190.

BUSECK, P. R. & IIJIMA, S. (1974). *Am. Mineral.* **59**, 1–21.

BUSECK, P. R. & IIJIMA, S. (1975). *Am. Mineral.* **60**, 771–784.

COWLEY, J. M. & IIJIMA, S. (1972). *Z. Naturforsch. Teil. A*, **27**, 445–451.

DUBEY, M., RAM, U. S. & SINGH, G. (1973). *Acta Cryst.* **B29**, 1548–1550.

DUBEY, M. & SINGH, G. (1978). *Acta Cryst.* **A34**, 116–120.

DUBEY, M., SINGH, G. & VAN TENDELOO, G. (1977). *Acta Cryst.* **A33**, 276–279.

JEPPS, N. W., SMITH, D. J. & PAGE, T. F. (1979). *Acta Cryst.* **A35**, 916–923.

MCCONNELL, J. D. M., HUTCHISON, J. L. & ANDERSON, J. S. (1974). *Proc. R. Soc. London Ser. A*, **339**, 1–12.

RAM, U. S., DUBEY, M. & SINGH, G. (1973). *Z. Kristallogr.* **137**, 341–351.

RAMSDELL, L. S. (1944). *Am. Mineral.* **29**, 431–442.

VAN LANDUYT, J., AMELINCKX, S., KOHN, J. A. & ECKART, D. W. (1973). *Mater. Res. Bull.* **8**, 1173–1182.

VAN LANDUYT, J., AMELINCKX, S., KOHN, J. A. & ECKART, D. W. (1974). *J. Solid State Chem.* **9**, 103–119.

VERMA, A. R. & KRISHNA, P. (1966). *Polymorphism and Polytypism in Crystals.* New York: John Wiley.

YESSIK, M., SHINOZAKI, S. & SATO, H. (1975). *Acta Cryst.* **A31**, 764–768.