

Inequivalent Sites and Multiple Donor and Acceptor Levels in SiC Polytypes

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There is now experimental evidence of three nitrogen donor levels in $6H$ SiC. The possibility of such multiple levels is a result of crystallographically inequivalent sites in the large unit cells of the common SiC polytypes. The existence of multiple levels indicates departures from the hydrogenic approximation. For x-ray scattering, the usual structure factor approximation, in which polytypes are considered as various stacking orders of *equivalent* planes, may be inadequate.

I. INTRODUCTION

THE previous paper¹ (CP) shows that there are three inequivalent nitrogen atoms in the $6H$ SiC samples examined. Nitrogen is known to substitute for carbon,² hence, we have evidence of three inequivalent carbon sites in $6H$ SiC. The recombination radiation of $15R$ SiC indicates the presence of 4, and possibly of 5 sites.³

The existence of several *sites*, not required to be equivalent by crystal symmetry, is possible only when the crystal unit cell is large, as it is in the most common SiC polytypes, $6H$, $15R$, and $4H$. The existence of several *ionization energies* for nitrogen donors in a SiC polytype requires, in addition, a departure from the hydrogenic model in the neighborhood of the nitrogen. Such departures from the hydrogenic approximation⁴ give rise to different ionization energies for chemically different donors and acceptors in Ge and Si. In the latter, however, the differences near chemically different impurity atoms are due to the impurity atoms themselves, whereas, in SiC polytypes, the differences near inequivalent nitrogen atoms are due to the crystallographic inequivalence of the substituted carbon atoms.

The recombination radiation of CP¹ originates in four-particle complexes (a nitrogen ion plus three electronic particles) whose dissociation energies, E_D , were found to be 16, 31, and 32.5 meV. Haynes⁵ found that, for a large number of impurities in Si, E_D is approximately one-tenth the impurity ionization energy, E_i . We do not know if such a relationship holds in $6H$ SiC, as the 3 values of E_i for nitrogen are not known. However, Haynes also gives an argument by Kohn which places E_D between $0.055E_i$ and $0.35E_i$ for any hydrogenic impurity in any host crystal. Thus, it seems probable that the values of E_i for nitrogen in $6H$ SiC will at least reflect the values of E_D in having one E_i considerably smaller than the other two.

The electron spin resonance experiments of Wood-

bury and Ludwig⁶ give direct information on the un-ionized nitrogen atoms in $6H$ SiC, and show the presence of 3 sites, although their resolving power permitted them only to distinguish one site from the other two. Thus, both exciton recombination and spin resonance experiments in $6H$ SiC suggest that one site is quite different from the other two. The unique site is not necessarily the same for both experiments, although it seems probable that it is.

In the next section, we shall consider the inequivalent sites in the common SiC polytypes, first in the approximation in which we consider the polytypes to be described by various stacking orders of equivalent close-packed atomic planes; and then, more accurately, by recognizing that the atomic planes differ in the same way that inequivalent sites differ, thus introducing a one-dimensional superstructure. The necessary modification of x-ray atomic scattering factors and structure factors will be discussed. Finally, measurements of the multiple donor and acceptor levels in SiC polytypes will be considered.

II. SiC POLYTYPES

A large number of SiC polytypes has been reported, many of which, having extremely large unit cells, are thought to owe their existence to the spiral growth mechanism.⁷ However, several polytypes, listed in Table I, appear to be equilibrium forms, although the conditions for their stability are not known. Correlations of polytypes and growth temperatures have been given,^{8,9} but it has not yet been possible, even with strict temperature control, to grow either $15R$ or $4H$ crystals without the presence of other polytypes.¹⁰ It has been suggested that impurities may influence the polytype.¹¹

There is some resemblance between SiC polytypes

¹ W. J. Choyke and Lyle Patrick, previous paper [Phys. Rev. **127**, 1868 (1962)].

² J. A. Lely, Ber. deut. keram. Ges. **32**, 229 (1955).

³ W. J. Choyke, D. R. Hamilton, and Lyle Patrick, Bull. Am. Phys. Soc. **7**, 185 (1962).

⁴ W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 257.

⁵ J. R. Haynes, Phys. Rev. Letters **4**, 361 (1960).

⁶ H. H. Woodbury and G. W. Ludwig, Phys. Rev. **124**, 1083 (1961).

⁷ F. G. Frank, Phil. Mag. **42**, 1014 (1951); S. Amelinckx and G. Strumane, in *Silicon Carbide*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, New York, 1960), p. 162; R. S. Mitchell, Z. Krist. **109**, 1 (1957).

⁸ H. Jagodzinski and H. Arnold, in *Silicon Carbide*, edited by J. R. O'Connor and J. Smiltens (Pergamon Press, New York, 1960), p. 136.

⁹ R. F. Adamsky and K. M. Merz, Z. Krist. **111**, 350 (1959).

¹⁰ D. R. Hamilton (private communication).

¹¹ D. Lundquist, Acta Chem. Scand. **2**, 177 (1948).

TABLE I. Some of the simple SiC polytypes, with three common notations.

Ramsdell notation	ABC notation	Jagodzinski notation	No. of inequivalent Si (or C) sites	Remarks
2H (wurzite)	AB	<i>h</i>	1	A rare polytype in SiC
3C (zincblende)	ABC	<i>k</i>	1	A low-temperature form of SiC
4H	ABAC	<i>hk</i>	2	
6H	ABCACB	<i>hkk</i>	3	The most common high-temperature polytype
15R	ABCACBCABACBCB	<i>hkkhk</i>	5	

and the "long-period superlattices" in CuAu recently investigated by Sato and Toth.¹² The energy discontinuities introduced by the superstructure apparently stabilize the phases of CuAu, but it is hard to see how this mechanism could be of any importance in a non-metal like SiC.

A. Approximation of Equivalent Planes

All SiC polytypes¹³ consist of two crystallographically equivalent interpenetrating sublattices, one of Si atoms and one of C. It is, therefore, usually sufficient to describe one of the sublattices. Every polytype, in first approximation, may be described by its sequence of close-packed planes, which are stacked perpendicular to a threefold or a sixfold axis. The stacking order is given by a repeating sequence of the letters *A*, *B*, and *C*, representing the three sites available in one sublattice. Lower case letters *a*, *b*, and *c* may be used if one wishes to refer to the second sublattice. This representation, given in column 2 of Table I, is explicit but cumbersome, and the polytypes are usually denoted instead by the Ramsdell notation of column 1, which is concise, but may sometimes be ambiguous. A full description of the polytypes and the notation is given in Verma's book.¹³

The number of crystallographically inequivalent sites, listed in column 4, is equal to the number of atoms per unit cell of one sublattice, except in the hexagonal polytypes, where it is one-half that number because of the presence of the operator 6_3 in the hexagonal space group $P6_3mc$.

Each atom, whatever the polytype or site, has tetrahedrally bonded first neighbors on the other sublattice. The first site differences are due to second neighbors (on the same sublattice as the site considered). This difference is one of configuration, and can be described by the Jagodzinski notation¹³ of column 3, in which *h* means a hexagonal type configuration of second neighbors, like that of atom *B* in the sequence *ABA*; and *k* means a cubic configuration, like that of atom *B* in the sequence *ABC*. The *h* site has second neighbors on the two *A* planes which are "eclipsed," whereas the *k* site has second neighbors on the *A* and *C* planes which are "staggered" when viewed along the

c axis. The three sites of 6H SiC in this notation are represented by *hkk*, suggesting that one is different from the other two. The two *k* sites are, of course, inequivalent, but it is necessary to go to third neighbors to see the difference.

It is tempting to identify the *h* site in 6H SiC with the 16 meV *P* site of the previous paper,¹ and the two *k* sites with the 31 and 32.5 meV *R* and *S* sites, thus ascribing the large energy difference to the difference in second-neighbor configurations, and the small *R*, *S* difference to the effect of third and higher neighbors. However, Woodbury and Ludwig (WL) suggested a different choice for the unique site in their paper,⁶ putting greater weight on a third-neighbor distance difference than on the second-neighbor configuration difference. The third neighbors are on the second sublattice, and in the sequence $A\tilde{a}Bb\tilde{A}a$ the \tilde{A} atom has a unique third neighbor \tilde{a} at a distance $5d$ in the WL notation, where $3d$ is the tetrahedral bond length, and $4d$ the Si or C interplanar spacing in the axial direction. In this sequence the *B* atom is *h* in Jagodzinski's notation, and it can be seen that, in any polytype, every *h* site must be accompanied by a WL site which is one of its second neighbors. For electron spin resonance, it may be possible to determine which is the markedly different site in 6H SiC by a double resonance experiment.¹⁴

B. Inequivalent Planes

The sequence of close-packed planes in 6H SiC may be thought of as *hkk*, or as *PRS*, using the site notation of CP for planes of atoms. The marked *P* site difference noted in CP must distinguish every third plane of carbon atoms in the 6H stacking sequence (and presumably every third plane of Si atoms also). Crystal symmetry requires the equivalence and regular spacing of every third plane in 6H SiC, but allows *P*, *R*, and *S* plane differences and interplanar distance differences (e.g., the *PR* and *RS* interplanar distances need not be identical). Thus, the *h*, *k* difference need not be strictly a configurational difference, but may involve some change in bond lengths. The crystal symmetries of other SiC polytypes permit similar inequivalences.

No effects due to inequivalent sites or planes had previously been observed in SiC polytypes. It is,

¹² H. Sato and R. S. Toth, Phys. Rev. **124**, 1833 (1961).

¹³ A. R. Verma, *Crystal Growth and Dislocations* (Butterworths Scientific Publications, Ltd., London, 1953), Chap. 7.

¹⁴ G. Feher, Phys. Rev. **114**, 1219 (1959).

therefore, understandable that the assumption of equivalent planes has been made in the past.⁸ Some possible manifestations of site and plane differences will be discussed in the following section.

III. SITE DIFFERENCES IN SiC POLYTYPES

A. Effects in X-Ray Analysis

The inequivalent nitrogen atoms observed in CP indicate that there are differences in valence electron distributions at the three carbon sites. The valence electrons interact with x rays more weakly than they interact with charge carriers and phonons. However, because the carbon core is small, the failure of the free carbon atomic scattering factor to determine the x-ray scattering of diamond can be measured.¹⁵ For Si the effect of bonding is small but still measurable. For accurate 6H SiC x-ray work one would require 3 different Si and C atomic scattering factors. In addition, a difference in interplanar spacings could make a difference in structure factor calculations.

No doubt these effects are small, but they may contribute to the reported disagreement between calculated and observed structure factors in SiC polytypes.⁸ The assumption of equivalent planes leads to the vanishing of certain structure factors (e.g., $F_{00,2}$ and $F_{00,4}$) which would not vanish for an accurate analysis.

¹⁵ L. Kleinman and J. C. Phillips, Phys. Rev. **125**, 819 (1962); S. Göttlicher and E. Wölfel, Z. Elektrochem. **63**, 891 (1959); R. Brill, *ibid.* **63**, 1088 (1959).

The corresponding "superstructure" lines do not seem to have been observed. However, the effects of the corresponding Fourier coefficients of the potential ($V_{00,2}$ and $V_{00,4}$) on phonon frequencies were noted in CP.

B. Multiple Donor and Acceptor Levels

The first extensive conductivity and Hall measurements on single crystals of SiC were made by Busch,¹⁶ and by Busch and Labhart,¹⁷ on commercial crystals, but both impurity content and polytype were uncertain. The measurements showed evidence of two energy levels, which may possibly correspond to the h and k levels of a single donor or acceptor in 6H SiC. Later measurements by Lely and Kroger¹⁸ on laboratory samples also suggested two levels in many of the crystals.

There is a need for better measurements on crystals of definite polytype and known impurity content. It may now be possible to make such measurements not only on 6H crystals, but also on 15R and 4H polytypes. To find *three* impurity levels for a donor or acceptor in 6H SiC, it will probably be necessary to make measurements, such as infrared absorption measurements, in which high resolution is possible.

¹⁶ G. Busch, Helv. Acta **19**, 167 (1946).

¹⁷ G. Busch and H. Labhart, Helv. Phys. Acta **19**, 463 (1946).

¹⁸ J. A. Lely and F. A. Kröger, in *Semiconductors and Phosphors*, edited by M. Schoen and H. Welker (Interscience Publishers, Inc., New York, 1958), p. 525.