^{29}Si and ^{13}C Magic Angle Spinning N.M.R. Spectra of Silicon Carbide Polymorphs

Gordon R. Finlay, J. Stephen Hartman,* Mary F. Richardson, and Barbara L. Williams
Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada

Hexagonal and cubic silicon carbide polymorphs give distinctive ^{29}Si and ^{13}C magic angle spinning n.m.r. spectra that can be related to the number of nonequivalent lattice sites in the structure and variations in the non-nearest-neighbour environment.

Silicon carbide exists in many crystalline modifications based on hexagonal α-SiC (wurtzite-type ZnS), and there is also a cubic β-SiC structure (diamond or zinc blende type). The complexity arises from the numerous stacking sequences in the crystal.[1] A search of the Inorganic Crystal Structure Database[2] shows that crystal structures of many polytypes have been determined. They differ in the number of crystallographically nonequivalent silicon and carbon atoms, although the silicon–carbon bond lengths are similar in all the forms. Hence high-resolution solid-state n.m.r. spectroscopy[3] has potential for the study of such systems. We now report that ^{29}Si and ^{13}C magic angle spinning n.m.r. (m.a.s. n.m.r.) is highly sensitive to fine points of lattice structure.

Figures 1(a) and 1(b) are ^{29}Si and ^{13}C m.a.s. n.m.r. spectra of the 6H hexagonal polytype[4] of silicon carbide. The three equally populated silicon environments give three well resolved ^{29}Si peaks of equal area at −13.9, −20.2, and −24.5 p.p.m. from tetramethylsilane. The three equally populated carbon environments, isostructural with the silicon environments, give an almost exact mirror-image of the ^{29}Si spectrum: three well-resolved ^{13}C peaks of equal area at 15.2, 20.2, and 23.2 p.p.m. from tetramethylsilane. The single silicon environment of the cubic form[5] gives a single ^{29}Si resonance at −18.3 p.p.m., intermediate between peaks of the hexagonal 6H form [Figure 1(c)]. Figure 1(d), with three ^{29}Si peaks of unequal intensity, was obtained from a hexagonal silicon

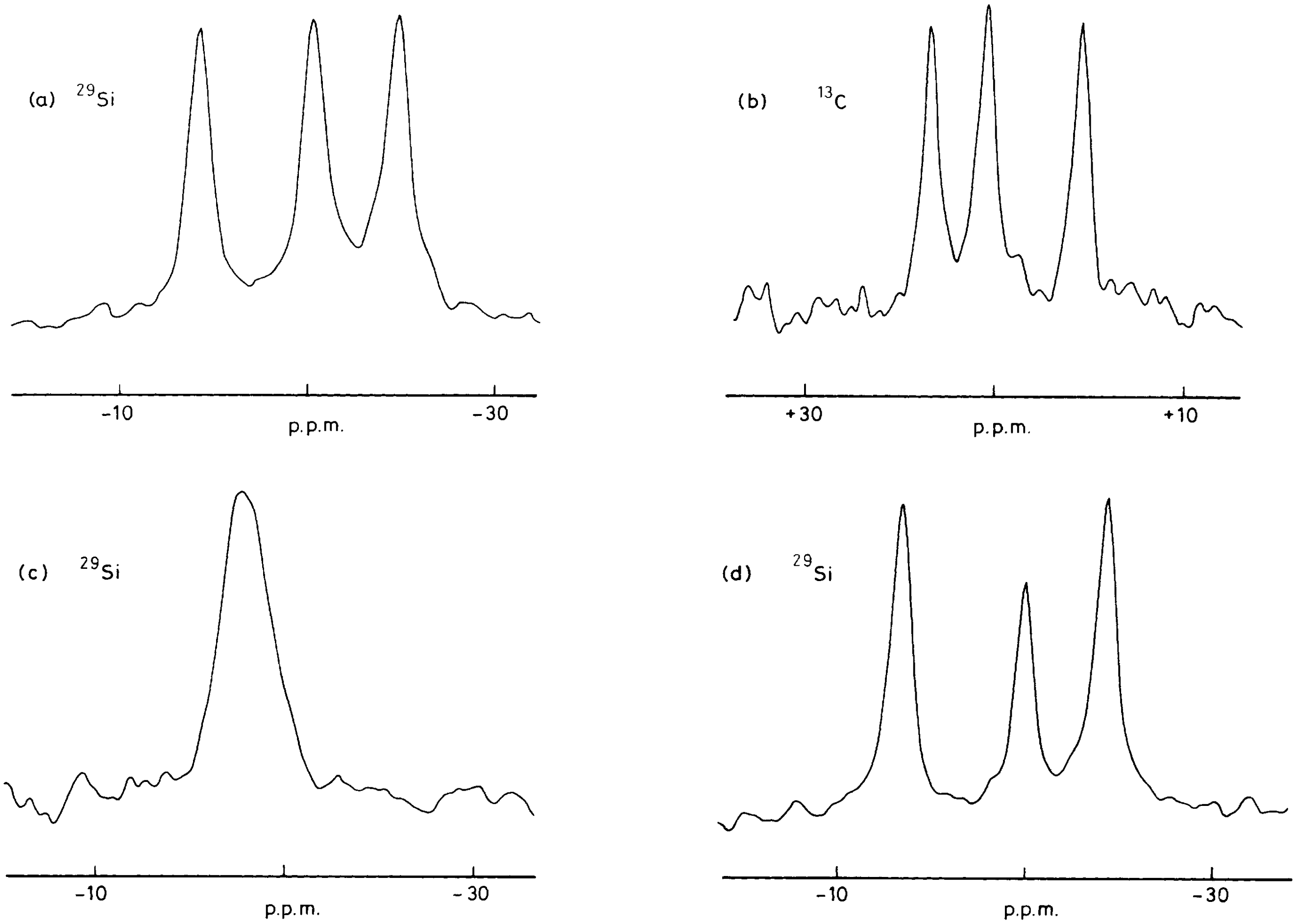

Figure 1. ^{29}Si and ^{13}C m.a.s. n.m.r. spectra of silicon carbide. (a) 6H polytype, ^{29}Si; (b) 6H polytype, ^{13}C; (c) cubic β-SiC, ^{29}Si; (d) mixture of polytypes, ^{29}Si.

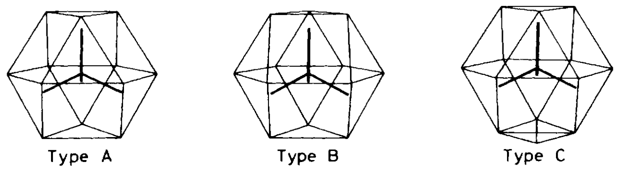

Figure 2. Silicon first and second neighbour environments in silicon carbide polytypes.

carbide sample which gave an *X*-ray powder pattern with lines additional to those of the 6H polytype.[5]

Examination of six silicon carbide polytypes of known structure (cubic, 4H, 6H, 8H, 15R, and 24R) shows that there are only three distinctive types of silicon environment, although there may be many crystallographically independent silicon positions. First and second neighbours of the three types are shown in Figure 2. The first neighbours of each silicon are four carbon atoms at the corners of a tetrahedron, but there are pronounced differences in the numbers and geometries of the second and higher neighbours. The 12 silicon second neighbours in Type A surroundings are located at the corners of a cuboctahedron. Type B silicon also has 12 silicon second neighbours, but one of the trigonal faces of the cuboctahedron is rotated through 60° to give an eclipsed 3–6–3 polyhedron. Type C silicon has 13 second neighbours: 12 silicon atoms at 3.08 Å and a carbon atom at 3.15 Å, with the overall shape being a cuboctahedron with one face capped by the carbon. The carbon environments mirror the silicon environments so that, for example, a Type C carbon atom has 13 second neighbours (12 C and 1 Si) at the corners of a capped cuboctahedron. Further distinctive polyhedra out to 5 Å are also characteristic of Types A, B, and C. Beyond 5 Å the geometry of more distant neighbours begins to diverge in the different polytypes, but such distant neighbours probably have little effect on chemical shift.

Cubic silicon carbide, with all silicon atoms crystallographically equivalent, contains only Type A silicon. The 6H form, a common hexagonal polytype with three independent silicon atoms, contains equal numbers of Types A, B, and C. Other polytypes present intriguing possibilities for m.a.s. n.m.r. spectroscopy; for example the 15R form,[5] with five independent silicon atoms, contains Types A, B, and C in a 1:2:2 ratio. Figure 1(d) indicates that, when a mixture of polytypes is present, Types A, B, and C silicon will be distinguishable by n.m.r. spectroscopy but individual polytypes need not be. Current n.m.r. studies of more complex polytypes should allow us to evaluate the importance of outer neighbours in determining the chemical shift, relative to the importance of minor variations in bond distances and angles in the inner spheres of silicon and carbon. In this context we note that the ^{29}Si chemical shift of the Type A silicon atoms of cubic silicon carbide is appreciably different from that of the Type A silicon atoms of the 6H polytype. In the 6H polytype one C–Si bond is slightly longer than the other three,[4] while in cubic silicon

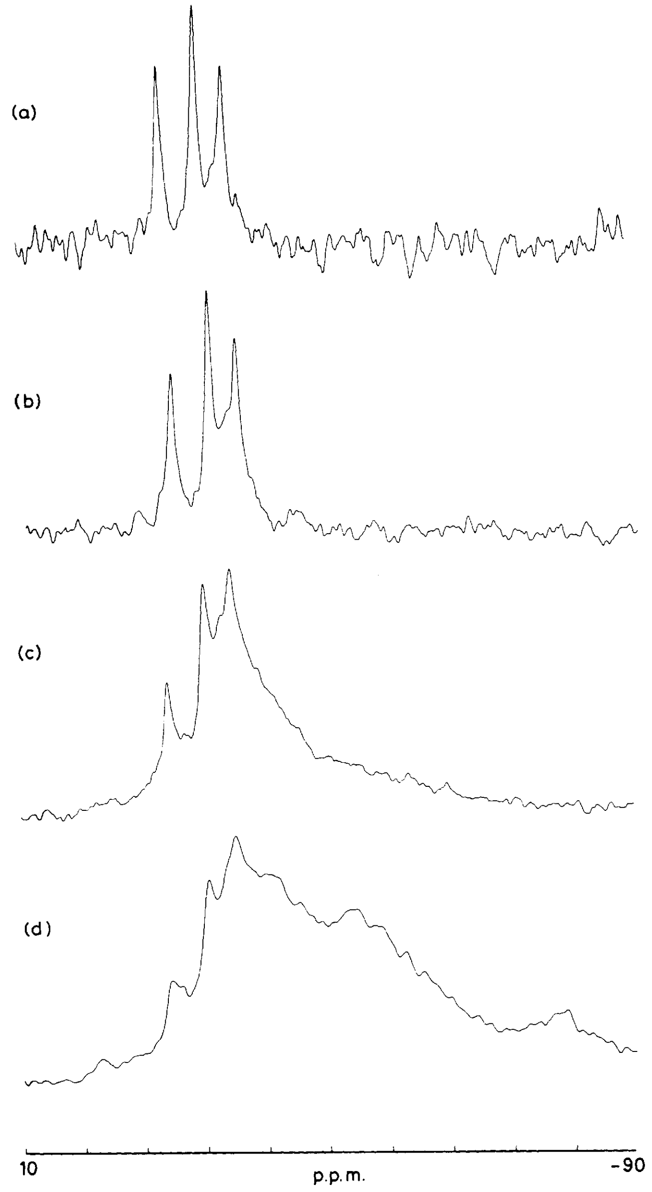

Figure 3. Effect of variation in relaxation delay between pulses on ^{29}Si m.a.s. n.m.r. spectra of a commercial sample of silicon carbide abrasive powder. Relaxation delays are: (a) 300; (b) 30; (c) 5; (d) 0.5 s.

carbide the symmetry is fully tetrahedral,[5] and this chemical shift difference may be due to nearest-neighbour effects.

Silicon carbide as prepared commercially is usually a mixture of polytypes,[6] and it is difficult to separate the various hexagonal forms. Individual well formed crystals can be separated manually but the use of X-ray diffraction and optical goniometry has been necessary to identify each individual crystal.[5] N.m.r. spectroscopy may provide a complementary approach to such systems. Caution must be exercised, however, as traces of paramagnetic impurities are often present. ^{29}Si and ^{13}C atoms near such impurities are likely to have especially short spin-lattice relaxation times.[7] If care is not taken to avoid saturation, the signal from such atoms can dominate the spectrum at the expense of atoms in the bulk structure, as illustrated in Figure 3. An insufficient relaxation delay between pulses greatly overemphasizes the contribution from traces of an apparently amorphous component. Our best-resolved spectra have been obtained using long relaxation delays (between 15 min and 4 h). It is of interest that our ^{29}Si and ^{13}C chemical shifts are in reasonable agreement with values obtained previously from non-m.a.s. single-peak spectra[8,9] but a discrepant ^{29}Si value of −69 p.p.m. is also reported,[8] outside the expected range for R_4Si compounds.[10] This spectrum may have been obtained under conditions that favoured a minor-component signal.

Since the pioneering work of Lippmaa *et al.* in 1980,[11] ^{29}Si m.a.s. n.m.r. spectroscopy has been extensively applied to aluminosilicates,[12,13] and in zeolites in particular has provided important structural information not available by other methods.[12] Recently detailed correlations of ^{29}Si chemical shifts with bond lengths and bond angles in aluminosilicates have been attempted.[14] A similar approach could be useful in the study of silicon carbide polytypes, and investigations along these lines are in progress. Our observation of apparently amorphous material in variable relaxation delay studies points to a probable major use of m.a.s. n.m.r. in the study of amorphous silicon carbide, a material that is coming into prominence as a high-temperature ceramic[15] but is intractable to most analytical techniques.

We thank the Natural Sciences and Engineering Research Council of Canada for financial support, Prof. C. A. Fyfe of the University of Guelph for providing the design of the magic angle spinning probe, Dr. Gordon Wood of SND-CISTI, National Research Council of Canada for access to the Inorganic Crystal Structure Database, Dr. R. E. Lenkinski, Mr. W. Klimstra, and Mr. A. G. Basile for technical assistance, and the Department of Geological Sciences, Brock University, for the use of equipment. The n.m.r. spectra were obtained at the South Western Ontario N.M.R. Centre, funded by a Major Installation Grant from N.S.E.R.C.

Received, 30th July 1984; Com. 1112

References

1 A. F. Wells, 'Structural Inorganic Chemistry,' 4th edn., Oxford University Press, Oxford, 1975, pp. 787—789.

2 G. Bergerhoff, R. Hundt, R. Sievers, and I. D. Brown, *J. Chem. Inform. Computer Sci.*, 1983, **23**, 66.

3 R. E. Wasylishen and C. A. Fyfe, *Annu. Rep. NMR Spectrosc.*, 1982, **12**, 1; C. A. Fyfe, 'Solid State N.M.R. for Chemists,' C. F. C. Press, Guelph, Ontario, 1983.

4 A. H. Gomes de Mesquita, *Acta Crystallogr.*, 1967, **23**, 610.

5 N. W. Thibault, *Am. Mineral.*, 1944, **29**, 327.

6 Kirk-Othmer, 'Encyclopedia of Chemical Technology', 3rd edn., vol. 4, Wiley, New York, 1978, pp. 520—535.

7 P. M. Henrichs, M. T. Cofield, R. H. Young, and J. M. Hewitt, *J. Magn. Reson.*, 1984, **58**, 85, and references therein.

8 G. R. Holzman, P. C. Lauterbur, J. H. Anderson, and W. Koth, *J. Chem. Phys.*, 1956, **25**, 172.

9 D. T. Haworth and C. A. Wilkie, *J. Inorg. Nucl. Chem.*, 1978, **40**, 1689.

10 H. Marsmann, in 'N.m.r. Basic Principles and Progress', vol. 17, eds. P. Diehl, E. Fluck, and R. Kosfeld, Springer-Verlag, Berlin, 1981, pp. 65—235; B. Coleman, In 'N.m.r. of Newly Accessible Nuclei', vol. 2, ed. P. Laszlo, Academic Press, New York, 1983, pp. 197—228.

11 E. Lippmaa, M. Mägi, A. Samoson, M. Tarmak, and G. Engelhardt, *J. Am. Chem. Soc.*, 1980, **102**, 4889.

12 C. A. Fyfe, J. M. Thomas, J. Klinowski, and G. C. Gobbi, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 259.

13 K. A. Smith, R. J. Kirkpatrick, E. Oldfield, and D. H. Henderson, *Am. Mineral.*, 1983, **68**, 1206, and references therein.

14 A.-R. Grimmer and R. Radeglia, *Chem. Phys. Lett.*, 1984, **106**, 262; J. V. Smith, C. S. Blackwell, and G. L. Hovis, *Nature (London)*, 1984, **309**, 140, and references therein.

15 H. J. Sanders, 'High-Tech Ceramics,' *Chem. Eng. News*, 9 July 1984, p. 26.