Molecular Structure of $C(GeBr_3)_4$ Determined by Gas-Phase Electron Diffraction and Density Functional Theory Calculations: Implications for the Length and Stability of Ge−C Bonds in Crystalline Semiconductor Solids

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The structure of $C(GeBr_3)_4$ has been determined by gas-phase electron diffraction. It has a C−Ge bond length of 2.042(8) Å (about 0.1 Å longer than normal), and the 12 Br atom positions are close to the vertices of a regular icosahedron. Density functional calculations closely reproduce the observed structure. The implications of the observed structure for bond lengths in Ge−C crystals and related electronic materials based on the diamond structure are discussed.

Introduction

There is currently considerable interest in preparing diamond-structure Ge−C solid solutions and compounds because of their potential interest as electronic materials.[1] Surprisingly, although SiC is a well-known stable phase and Si and Ge form continuous solid solutions, the mutual solubility of C and Ge is extremely small, and the compound GeC is predicted[2] to be metastable with respect to disproportionation into the elements. In fact, no inorganic crystal structure with Ge−C bonds appears to have been reported[3] although metastable dilute solutions of C in Ge have been grown by molecular beam epitaxy.[4] Recently heteroepitaxial layers of Ge−C with up to 7 atom % C were grown on Si by chemical vapor deposition (CVD) techniques.[5] The sphalerite (ZnS) related compound $GeSi_3C_4$ has also been grown in polycrystalline form by CVD.[6]

One of the reasons for the interest in Ge−C alloys is the observation that the lattice parameter of Si ($a = 5.430$ Å) is intermediate between that of Ge ($a = 5.657$ Å) and diamond ($a = 3.567$ Å) so that Ge doped with a suitable level of C should exactly match the lattice parameter of Si and allow strain-free heteroepitaxial layers of Ge−C to be grown on single crystals of Si. In this connection it is sometimes assumed that the lattice parameter of an intermediate phase may be obtained by linear interpolation between those of the pure components (Vegard's law); in particular, it is proposed[7] that Si−Ge−C alloys with a Ge/C ratio of 8.2/1 will produce material with a dimensional match to pure Si. The results for Ge−C bond lengths described in this paper cast serious doubts on that assumption and suggest that some of the results for C alloyed with Ge and/or Si should be re-examined without the assumption of Vegard's law applying.

The CVD preparations of Ge−C materials utilized molecular precursors with Ge−C bonds such as $CH_n(GeH_3)_{4-n}$ ($n = 0-3$). These were prepared[5] by $LiAlH_4$ reduction of the corresponding halides $CH_n(GeX_3)_{4-n}$ (X = Cl, Br). The halides in turn were prepared[5,8] by insertion of GeX_2 into the C−X bonds of CH_nX_{4-n}. An investigation[8] of the structure of crystalline $C(GeBr_3)_4$ showed that the molecules were disordered in the solid state and had an average arrangement close to icosahedral symmetry. The derived Ge−C bond lengths of 2.01−2.05 Å were substantially longer than normal Ge−C bond lengths which are close to 1.945 Å in carbogermanes; examples are d(Ge−C) = 1.945(3) Å in $Ge(CH_3)_4$,[9a] 1.947(6) Å in $GeH(CH_3)_3$,[9b] 1.950(3) Å in $GeH_2(CH_3)_2$,[9c] and 1.9453(3) Å in GeH_3CH_3.[9d] The unusual bond lengths found in $C(GeBr_3)_4$ suggest that molecules (and crystals) with a central C bonded to four Ge groups might be sterically crowded; accordingly, we have undertaken a precise determination of the molecular structure of $C(GeBr_3)_4$ by gas-phase electron diffraction (GED).

Experimental Section

$C(GeBr_3)_4$ was prepared as earlier described.[8] Gas-phase electron diffraction data were recorded on the Balzers KDG2 unit at Oslo[10] with a metal inlet system and sample reservoir at 218 °C. Exposures were made with the nozzle-to-plate distances of about 25 cm (five plates) and 50 cm (six plates). The plates were scanned on an Agfa Arcus II

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Table 1. Interatomic Distances (r) and Root-Mean-Square Vibrational Amplitudes (l) in Angstroms, Observed (GED) and Calculated (DFT) for C(GeBr$_3$)$_4$, Bond and Torsion Angles in Degrees

	GED		DFT
	r	l	r
C−Ge	2.042(8)	0.12(3)	2.051
Ge−Br	2.282(3)	0.061(2)	2.297
Ge···Ge	3.33(1)	0.13(1)	3.348
C···Br	3.61(1)	0.08(5)	3.627
Br···Br[a]	3.64(1)	0.16(2)	3.663
Ge···Br	3.77(2)	0.16(1)	3.873
Ge···Br	4.58(2)	0.32(3)	4.490
Ge···Br	5.32(1)	0.17(1)	5.386
Br···Br	3.48(6)	0.70(20)	3.926
Br···Br	4.11(4)	0.28(3)	3.909
Br···Br	6.03(2)	0.21(3)	6.170
Br···Br	6.12(2)	0.39(5)	6.203
Br···Br	6.33(4)	0.44(16)	6.103
Br···Br	7.20(2)	0.24(4)	7.252
$\angle$(C−Ge−Br)	112.9(5)		112.9
$\angle$(Br−Ge−Br)	105.9(5)		105.8
τ(Ge−C−Ge−Br)	31.4(9)		38.6

[a] Within a CBr$_3$ group.

scanner, and the data were processed as described elsewhere.[11] Atomic scattering factors were taken from ref 12. Backgrounds were drawn as least-squares polynomials adjusted to the difference between the total experimental and the calculated molecular intensities. The molecular structure was refined by least-squares calculations on the intensity data using the program KCED 26 written by G. Gundersen, S. Samdal, H. M. Seip, and T. G. Strand. The structure refinement of C(GeBr$_3$)$_4$ was based on a molecular model of T symmetry characterized by four independent parameters: the Ge−C and Ge−Br bond distances, the C−Ge−Br bond angle, and the torsion (dihedral) angle τ(Ge−C−Ge−Br). All root-mean-square vibrational amplitudes were refined. Vibrational correctional terms were not included. The R factors were calculated as $R[\sum(I_o - I_c)^2/\sum I_o^2]^{1/2}$. For the 25 cm data $R = 3.6\%$, for the 25 cm data $R = 8.8\%$, and overall $R = 5.6\%$. The refinements converged to yield the structure parameters listed in Table 1. The refinements were carried out with diagonal weight matrices so the estimated standard deviations have been doubled to allow for data correlation as discussed by Seip et al.[13] and expanded to include a scale uncertainty of 0.1%.

Results

Shown in Table 1 are the results also of a theoretical study of the equilibrium molecular geometry by density functional theory (DFT) using the program system Gaussian 94.[14] The calculations were carried out with the LanL2DZ basis set[15] and employed the gradient correction of Becke[16] for exchange and of Perdew and Wang[17] for correlation. This level of calculation represents the state-of-the art for molecules with this many electrons (560) and can be expected to yield results close to the correct values. The agreement between theory and experiment is very good, particularly when allowance is made for the fact that the theoretical calculation does not allow for thermal or even zero-point displacements (which could affect especially the torsion angle τ). Certainly it is good enough to reassure us that nothing has gone catastophically wrong with the experiment.

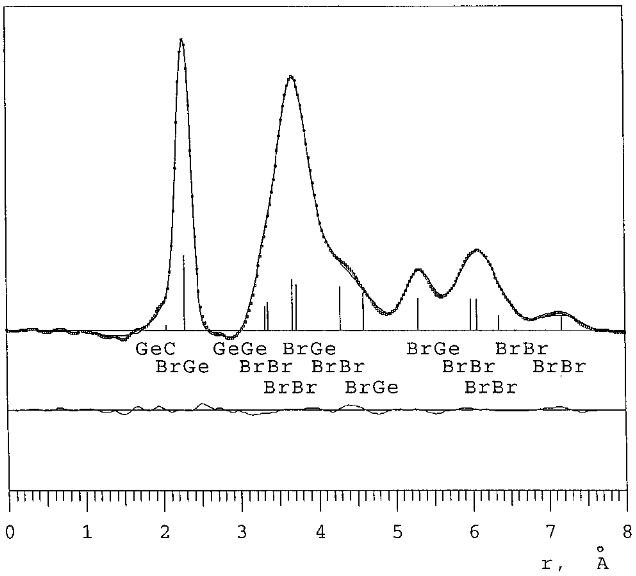

Figure 1. Top: modified experimental (dots) and calculated (full lines) molecular intensity curves for C(GeBr$_3$)$_4$ of T symmetry. Bottom: difference curves. Artificial damping constant: 0.0025 Å^2.

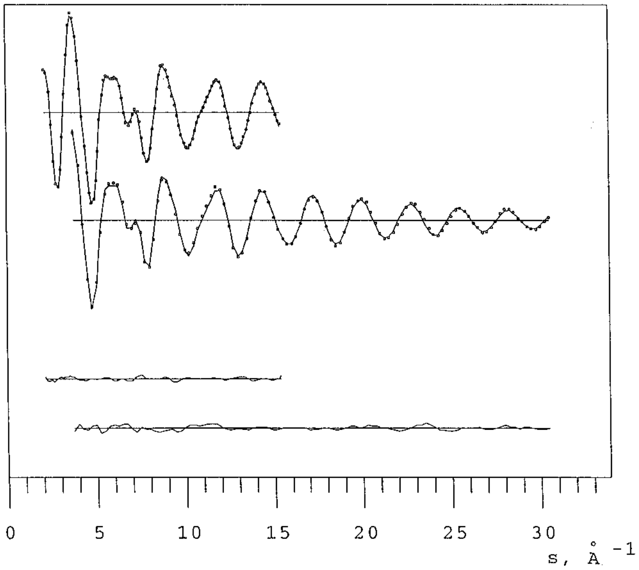

Figure 2. Top: experimental (dots) and calculated (line) radial distribution functions for C(GeBr$_3$)$_4$. Bottom: difference curve.

Experimental and calculated molecular intensity curves are compared in Figure 1, and experimental and calculated radial distribution curves are shown in Figure 2. The structure of the molecule is illustrated as a ball-and-spoke model in Figure 3 , and the Br packing is illustrated in Figure 4.

Discussion

There are two striking features of the structure of C(GeBr$_3$)$_4$ to which we call special attention.

First, the remarkably long C−Ge bond length found by X-ray diffraction of disordered crystals is confirmed, both in the experimental molecular structure and in the density functional

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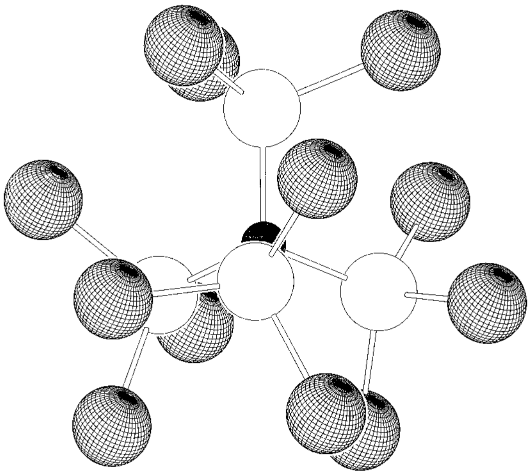

Figure 3. Molecular model of $C(GeBr_3)_4$ with *T* symmetry.

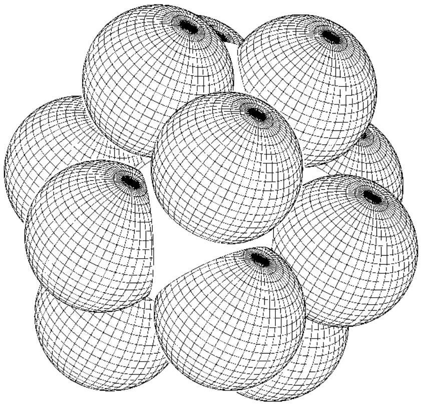

Figure 4. Packing model of the Br atoms in $C(GeBr_3)_4$. Notice that each Br has five Br neighbors in an icosahedral arrangement.

calculation. It is fully 0.10 Å longer than in typical carbogermanes and is symptomatic of a weakened bond, presumably due to steric strain. Elongation (by smaller amounts) of the central C−Si bond in $C(SiMe_3)_4$[18] and the central C−Sn bond in $C(SnMe_3)_4$[19] has been ascribed to similar causes.

Second, as should be apparent from Figure 4, the arrangement of Br atoms is close to icosahedral. To be exactly icosahedral, the first three Br···Br distances listed in Table 1 would be equal and the torsion angle, τ, would be 37.8°. For a given C···Br distance (i.e., distance from the center of the molecule), an icosahedral arrangement of the 12 Br atoms maximizes the Br···Br distances, and presumably this is the reason for this geometry. Comparison with the bond distances in GeH_2Br_2 [2.277(3) Å][20a] and $GeBr_4$ [2.272(3) Å][20b] indicates that the Ge−Br bond distances in $C(GeBr_3)_4$ [2.283(3) Å] are normal.

It is instructive to compare the structure of the molecule with an element of a crystal structure derived by an ordering of the diamond structure. We consider the simple case of a cubic ordered structure AB_4C_3; this is a possible structure for the composition Ge_7C ($A = C$, $B = C = Ge$). In Figure 5 we show a fragment AB_4C_{12} [$=A(BC_3)_4$] of this structure with the central *A* atom at the center of a cubic unit cell with symmetry $P\bar{4}3m$.[21]

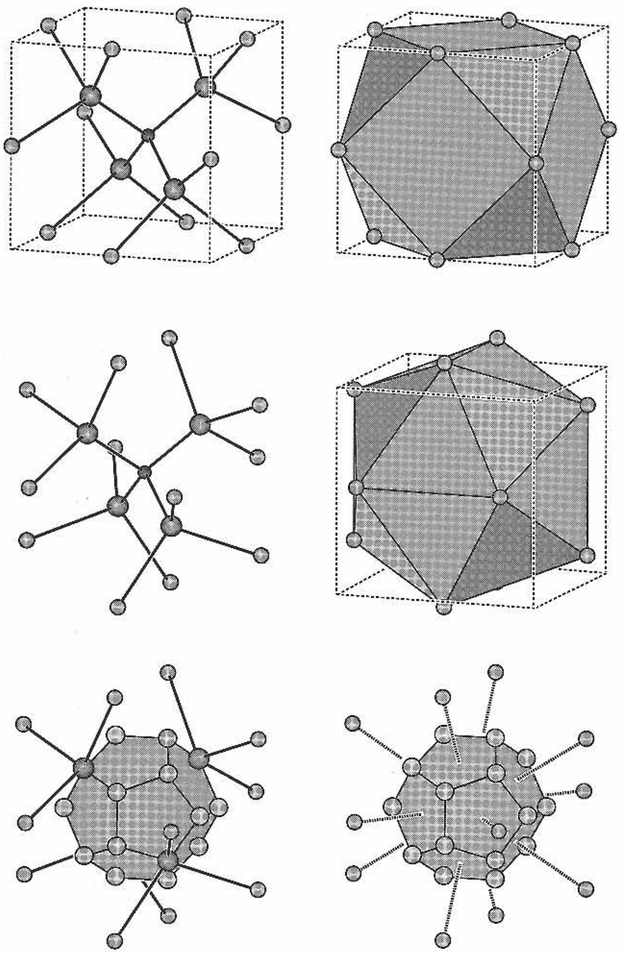

Figure 5. Top: left, a $P\bar{4}3m$ unit cell of an AB_4C_3 ordered version of the diamond structure; right, the cuboctahedral arrangement of the *C* atoms on the left. Middle: left, an $A(BC_3)_4$ molecule with the geometry of $C(GeBr_3)_4$; right, the icosahedral arrangement of the *C* atoms. Bottom: left, the BC_3 groups of the molecule above with (lighter-shaded larger circles) alternative positions of the *B* atoms; right, the structure of $C(GeBr_3)_4$ as determined by X-ray diffraction—the larger circles at the vertices of a dodecahedron correspond to sites with $^1/_5$ occupancy by Ge.

The 12 *C* next nearest neighbors of the central *A* atom are at the vertices of a cuboctahedron. As shown in the figure, rotation of triangular C_3 groups about the $B-C$ bond axis can convert from a cuboctahedron ($\tau = 0°$) to an icosahedron ($\tau = 37.8°$) of C_{12}. Thus, it may be seen that the crystal contains $A(BC_3)_4$ units but the constraints of symmetry require the more strained cuboctahedral C_{12} geometry (with T_d symmetry for the AB_4C_{12} fragment) in contrast to the molecule with icosahedral shape (*T* symmetry). Accordingly even longer C−Ge bond lengths might be expected in diamond-related $Ge_{1-x}C_x$ crystals.[22]

The icosahedral shape found for the molecule also explains the earlier crystallographic observations.[8] Within the icosahedral shell of Br atoms, there are 20 equivalent positions, at the vertices of a dodecahedron, for the Ge to be bonded to three Br atoms. (The requirement of tetrahedral geometry for the central CGe_4 unit splits these 20 positions into 5 groups of 4.) At the

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[21] The cubic structure is described in ref 2b as that of luzonite, $Cu_3(As,Sb)S_4$, but in fact that mineral has a different tetragonal structure: Marumo, F.; Nowacki, W. *Z. Kristallogr.* **1967**, *124*, 1.

[22] Since this paper was completed, the results of some relevant *ab initio* density functional theory calculations on clusters have been published. In these clusters, a central C atom is surrounded by either 34 or 70 Ge atoms, forming a fragment of the diamond structure that is terminated on the outside by H atoms. The C−Ge bond lengths are indeed found to be lengthened from normal and are 2.018 and 2.046 Å in the smaller and larger clusters, respectively: Hoffman, L.; Bach, J. C.; Nielsen, B. B.; Leary, P.; Jones, R.; Oberg, S. *Phys. Rev. B* **1997**, 11167.

bottom left of Figure 5 we show the dodecahedron of Ge positions, and at the bottom right, the structure determined by X-ray diffraction.

We note that the idea of steric repulsion elongating bonds and reducing the stability of tetrahedral molecules such as that studied here is not new. In 1981 Toman et al.[23] remarked, "one suspects that $C(SiH_3)_4$ and $C(GeH_3)_4$ might not be stable for simple steric reasons". In fact they are stable, and their utility as precursors in producing novel diamond-structure phases has been demonstrated, but for the reasons outlined in this paper, we expect to find unusual bond lengths in such materials.

Finally, we comment on the applicability of Vegard's law in estimating the Ge−C composition that will match the lattice parameter of Si. Linear interpolation between the unit cell parameters of C (diamond) and Ge leads to a ratio Ge/C = 8.2.[7] However, a "normal" Ge−C bond length (as detailed in the Introduction) of 1.945 Å would result in a unit cell edge of a = 4.492 Å for (so far unknown) GeC and linear interpolation between this composition and elemental Ge results in a lattice match with Si at Ge/C = 9.3. On the other hand, a Ge−C bond length of 2.05 Å such as found in this work produces a = 4.734 Å and the matching composition of Ge/C = 7.1. Clearly, even if linear interpolations were valid, the appropriate relationship between unit cell edge and composition in Ge−C alloys remains very uncertain.

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