

Observation of a Simple-Cubic Phase of GaAs with a 16-Atom Basis (SC16)

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(Received 17 February 1998)

An SC16 phase of GaAs has been observed at high pressure. The phase is obtained by heating the high-pressure *Cmcm* phase to above ~ 400 K at ~ 14 GPa and is found to be stable on cooling back to room temperature. The detailed structure has been refined. On pressure decrease, the SC16 phase is found to be stable down to atmospheric pressure. From high-temperature studies, the equilibrium range for the SC16 structure is 13 to 14.5 GPa. [S0031-9007(98)06381-9]

PACS numbers: 61.50.Ks, 62.50.+p

On pressure decrease from their high-pressure β -tin phases, Si and Ge transform back not to the diamond structure, but to more complex metastable structures denoted BC8 (body-centered cubic with an 8-atom basis), R8 (rhombohedral with an 8-atom basis) [1,2], and ST12 (simple tetragonal with a 12-atom basis) [3]. These phases have attracted considerable attention from theoreticians [4–10] both because of their intrinsic interest, and because the topology of the distorted-tetrahedral bonding is similar to that proposed for grain boundaries and surface reconstructions in Si [8]. These complex tetrahedral structures also provide computationally tractable models for studying how amorphous structures develop from increasing short-range disorder in the crystalline phase [5].

It would be of great interest if similar phases existed in III-V or II-VI systems, and, indeed, calculations using the binary equivalent of the BC8 structure in GaAs [11], denoted SC16 (simple cubic with a 16-atom basis), were performed over 20 years ago [12]. More recently, *ab initio* calculations have been used to consider the stability of the SC16 phase in a number of III-V systems. Crain *et al.* [13] reported that the SC16 structure is stable in GaAs, InAs, and InSb at high pressure, and calculated that the zinc blende (ZB) to SC16 transition in GaAs should occur at the surprisingly low pressure of 2.0 GPa [13]. Subsequent calculations by Mujica *et al.* [14] confirmed SC16 to be an equilibrium phase of GaAs, but reported a ZB-to-SC16 transition pressure of 11.5 GPa. They also found that SC16 itself would transform to the orthorhombic *Cmcm* structure at 12.7 GPa [14]. The higher value for the ZB-to-SC16 transition pressure in GaAs was supported in further calculations by Crain *et al.* [15], who, using more extensive *k*-point sampling than in their earlier study, obtained a transition pressure of 10.9 GPa.

However, despite these results, and further recent calculations which report that the SC16 structure should be stable also in GaP from 14.7 to 20.3 GPa [16], there has been no experimental evidence of the SC16 phase in any III-V or II-VI semiconductor to date. Crain *et al.* [13] suggested that transitions to the SC16 phase are kinetically inhibited by the requirement that no like-atom bonds are formed—a problem that does not arise in

monatomic Si and Ge. Indeed, the SC16 structure *has* been observed in the more ionic I-VII systems CuCl and CuBr [17] where the kinetic barriers are lower [13].

As part of a systematic study of the high-pressure behavior of the III-V, II-VI, and group IV semiconductors, we have made high-temperature high-pressure diffraction studies of GaAs. We find that the SC16 phase can be obtained by moderate heating of the *Cmcm* phase at pressures of ~ 14 GPa. The SC16 phase is stable on reducing temperature back to ambient and can be recovered to ambient pressure.

The samples of GaAs were a finely ground powder obtained from starting material of 99.9999% purity. Diffraction data were collected on station 9.1 at the Synchrotron Radiation Source, Daresbury Laboratory, using an image-plate area detector [18]. The incident wavelength was 0.4654(1) Å. The samples were loaded into Merrill-Bassett and Diacell DXR5 diamond-anvil cells (DACs) with 4:1 methanol:ethanol as a pressure transmitting medium and chips of ruby for pressure measurement. *In situ* high-temperature measurements were made by resistively heating the entire pressure cell. The sample temperature was obtained from a thermocouple attached to the gasket and is accurate to better than ± 5 K. Structural information was obtained from Rietveld refinement of the integrated profiles using the program MPROF.

Evidence for SC16 was first observed during attempts to sharpen *Cmcm*-phase profiles by heating. Figure 1 shows a series of diffraction profiles obtained on heating to 448 K in a Merrill-Bassett DAC, starting with *Cmcm*-GaAs at a pressure of 18 GPa. Heating below 373 K produced only a drop in sample pressure. Slightly higher temperatures—profiles (d) and (e)—produced the considerably sharper *Cmcm*-phase diffraction patterns that were sought. However, further heating to 423 K resulted in the appearance of new reflections, as marked by dots below profile (f). These additional peaks were found to remain on reducing the sample temperature back to ambient—as marked by arrows in profile (h)—but the cooling of the pressure cell produced a further reduction in sample pressure to 10.5 GPa. Because this pressure is below that at which the *Cmcm* phase transforms to ZB and cinnabar [19], profile

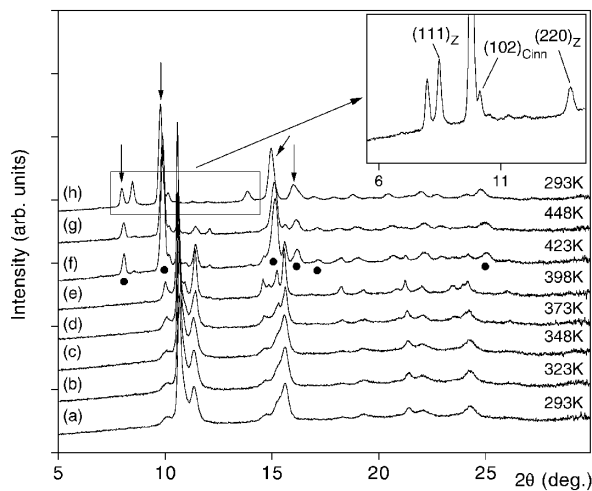


FIG. 1. Diffraction profiles obtained on heating a sample of *Cmc* GaAs to 448 K starting at a pressure of 18 GPa. The dots below profile (f) mark the positions of new reflections appearing at 423 K. These reflections remain on cooling back to ambient temperature—as marked by arrows in profile (h). The inset shows an enlargement of the low-angle region of profile (h), with the most intense reflections from the zincblende (Z) and cinnabar (Cinn) phases indexed.

(h) is a mixture of SC16 with both these phases—as shown in the inset. From the peak positions of the *Cmc* phase in profiles (e) and (f), we can estimate that the sample pressure was 13.5(5) GPa when SC16 first appeared, at an estimated temperature of 410(13) K.

Subtraction of the ZB- and cinnabar-phase peaks from profile (h) in Fig. 1 yielded a simple diffraction profile very similar to that we have observed previously from the BC8 phases of Si and Ge [20]. Refinements showed that all the peaks from the new phase could indeed be indexed on a cubic unit cell and that the peak intensities were consistent with those expected from the SC16 structure. However, these refinements revealed that the three-phase nature of the profile hampered detailed refinement of the SC16 structure, and that better quality diffraction profiles were required.

As the SC16 phase is stable at ambient temperature, all further diffraction studies of the SC16 phase were made at room temperature (RT) on samples that had previously been heated in an off-line furnace. As the Merrill-Bassett DAC used in the *in situ* study lost considerable pressure on heating, these further studies were made in Diacell DXR5 DACs which lost only ~ 0.2 GPa on heating. Results showed that if the sample pressure remains above 14.5 GPa at high temperature (HT), the only effect of heating is to sharpen the diffraction profiles from the *Cmc* phase. If the pressure at HT is below 14.5 GPa but above 13 GPa, samples transform to the SC16 phase. If the sample pressure at HT falls below 13 GPa, the diffraction profiles are dominated by peaks from the cinnabar and ZB phases, with only a small proportion of the SC16 phase being present. The highest-quality SC16 profiles were obtained by heating *Cmc* samples at 13.8(4) GPa to

~ 460 K, the maximum temperature available using the Diacell DAC. Such profiles still contain (weak) peaks from the *Cmc* phase, and it is likely that single-phase SC16 profiles could be obtained by heating the *Cmc* phase to temperatures above that obtainable using the beryllium-seat DACs employed in this study.

Before presenting a detailed analysis of the diffraction data for the SC16 phase, some discussion of the symmetry of the BC8 and SC16 structures is required. Since the initial discovery of the BC8 structure in Si, the structure has been described using spacegroup *Ia3* with an atom on the 16(c) position at (x, x, x) with $x \sim 0.1$ [1]. However, an *identical* structure is obtained with $x \sim 0.15$. In both cases the structure has centers of inversion symmetry at $(0, 0, 0)$ and $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. With the $x \sim 0.1$ description, the inversion center at $(0, 0, 0)$ must disappear in the SC16 structure to enable the bonded atoms at $(0.1, 0.1, 0.1)$ and $(-0.1, -0.1, -0.1)$ to be of different atomic species; this appears to have misled Crain *et al.* [13] into concluding that the SC16 structure has the noncentrosymmetric spacegroup *P2₁3*. In fact, the SC16 structure still contains a center of inversion at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the true symmetry is *Pa3*. This second set of inversion centers was noted by Mujica *et al.* [14] and the *Pa3* symmetry is supported experimentally by Hull and Keen [17]. In spacegroup *Pa3* one atomic species is on the 8(c) position at (u, u, u) with $u \sim 0.15$ while the other is on another 8(c) site at (v, v, v) with $v \sim 0.65$. Although the $x \sim 0.1$ and $x \sim 0.15$ descriptions of the BC8 structure are identical, the relationship between the BC8 and SC16 structures is greatly simplified if the $x \sim 0.15$ description of BC8 is used, because this allows both structures to be described with respect to a common origin. The transition from BC8 to SC16 then results in the loss of the inversion center at $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the atoms at $(0.15, 0.15, 0.15)$ and $(0.35, 0.35, 0.35)$ are bonded to each other in both structures.

Figure 2 shows a mixed SC16/*Cmc* profile obtained by heating *Cmc* GaAs at 13.8 GPa and 453 K for 48 min before cooling to RT and raising the pressure to 18.9 GPa [21]. The SC16 profile comprises strong $h + k + l = \text{even}$ reflections and much weaker $h + k + l = \text{odd}$ reflections which are absent in profiles from the body-centered BC8 structure. This second class of reflections, the strongest of which are enlarged and indexed in the inset to Fig. 2, shows the SC16 structure to be site ordered, and provides critical information on the values of u and v : if $v - u = \frac{1}{2}$ then the SC16 structure is pseudo body-centered and the intensity of the $h + k + l = \text{odd}$ reflections depends only on the difference in scattering power of the Ga and As atoms, while if $v - u \neq \frac{1}{2}$ there will be an additional structural component. As shown in Fig. 2, the Rietveld fit to the SC16/*Cmc* profile is excellent, with $R_I = 2.50\%$ and $R_{WP} = 4.72\%$. The best fit to the low-angle weak reflections is shown enlarged in profile (b) of the inset. Trial refinements with $v - u$ constrained to be equal to $\frac{1}{2}$ gave significantly less intense

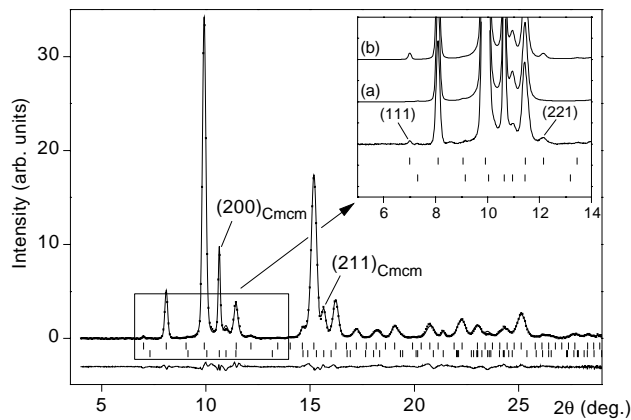


FIG. 2. Rietveld refinement fit to a mixed SC16/ $Cmcm$ profile at 18.9 GPa and 298 K. The upper (lower) tick marks show the positions of all reflections allowed by symmetry in the SC16 ($Cmcm$) phase. The difference between the observed and calculated profiles is shown below the tick marks. The strongest $Cmcm$ phase peaks are indexed in the main profile. The best fit to the low-angle weak reflections is shown enlarged in profile (b) of the inset, while profile (a) shows the best-fitting profile with $v - u$ constrained to be equal to $\frac{1}{2}$.

$h + k + l = \text{odd}$ reflections [profile (a) in the inset], confirming directly that $v - u \neq \frac{1}{2}$.

The refined lattice parameters are $a = 5.017(1)$ Å, $b = 5.325(1)$ Å, and $c = 4.862(3)$ Å for $Cmcm$ [$V/V_0 = 0.719(1)$] and $a = 6.594(1)$ Å for SC16 [$V/V_0 = 0.793(1)$]. The relative volume of the ZB phase at the same pressure is 0.844 [22], and thus the SC16 phase is 5.1(1)% denser than ZB, and 7.4(1)% less dense than $Cmcm$ at 18.9 GPa. The theoretical relative volume of the SC16 phase at 18.9 GPa—obtained from the calculated values of B_0 and B' [14]—is 0.776, giving a calculated lattice parameter (from the experimental value of V_0) of 6.546 Å, only 0.7% smaller than that observed.

The atomic coordinates for the SC16 phase at 18.9 GPa are $u(\text{Ga}) = 0.152(1)$ and $v(\text{As}) = 0.640(1)$, so that $v - u = 0.488(1)$. The recent calculations on SC16-GaAs have used a different description of the structure from that used here [13,14], and a linear extrapolation of the results of Mujica *et al.* [14] to $V/V_0 = 0.793$ gives (in their notation) $x_1(\text{Ga}) = 0.0952$ and $x_2(\text{As}) = 0.1115$. In our notation, these are equivalent to $u(\text{Ga}) = 0.1548$ and $v(\text{As}) = 0.6385$, in excellent agreement with the experimental values.

The refined SC16 structure is shown in Fig. 3. As in the BC8 structure, each atom has one so-called A bond along the (111) axis and three so-called B bonds. In SC16-GaAs at 18.9 GPa, the A bondlength is 2.376(9) Å and the B bondlength is 2.365(9) Å. This compares with 4 unlike nearest neighbors at 2.313 Å in the zincblende structure at the same pressure [22]. Although each atomic species in the SC16 structure has the same bonding arrangement to its unlike nearest neighbors, the distances to the like-atom next-nearest neighbors (nnn) are different—3.472(9) Å for Ga and 3.198(9) Å for As. In the BC8 structure, these dis-

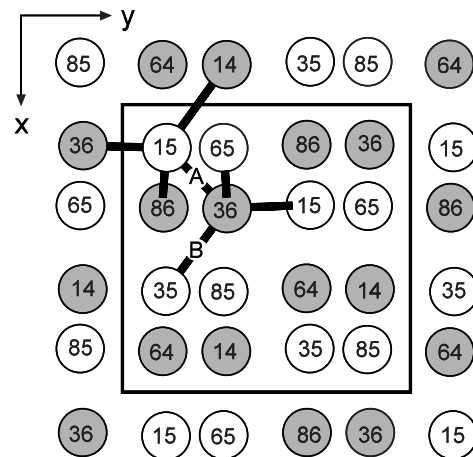


FIG. 3. The SC16 structure of GaAs, shown in projection down the z axis. Ga is at $(u \sim 0.15, u, u)$ and As is at $(v \sim 0.64, v, v)$. The numbers on each atom give the z coordinate in units of 0.01. Some of the short nearest-neighbor A and B bonds are shown.

tances are the same and become the so-called R_5 bond at the transition to R8 [13]. This difference in the nnn distances arises as a consequence of $v - u \neq \frac{1}{2}$, and means that interchange of the atomic species—such that $u(\text{Ga}) = 0.640$ and $v(\text{As}) = 0.152$ —results in a different structure where the nnn distance for As is longer than that for Ga. Because $v - u \sim \frac{1}{2}$ and because of the very similar scattering power of Ga and As, the two different structures produce diffraction patterns too similar to distinguish decisively. This problem was also noted in CuCl and CuBr by Hull and Keen [17], and in that case the distinction between the two structures was made on the basis that one results in unphysically short Cl-Cl and Br-Br distances. Trial refinements of SC16-GaAs using the second possible atomic arrangement—with As-As > Ga-Ga—did give a slightly poorer overall fit to the diffraction data ($R_I = 2.55\%$ and $R_{WP} = 4.74\%$), and, in particular, a poorer fit to the weak $h + k + l = \text{odd}$ reflections at low angles. Furthermore, Ga-Ga is expected to be greater than As-As because the structure is covalently bonded and Ga has the larger covalent radius [23]. This is supported by the calculations of Crain *et al.* [13] and Mujica *et al.* [14] which both find Ga-Ga > As-As. In both calculations, the other configuration was explicitly tested and found to have a higher energy [23].

We have also studied the apparent stability range of SC16-GaAs at room temperature (RT). We observe no transition from the SC16 phase down to ambient pressure (AP), where refinements of the SC16 structure give $a = 6.934(2)$ Å [$V/V_0 = 0.923(1)$] with $u(\text{Ga}) = 0.157(2)$ and $v(\text{As}) = 0.643(2)$, so that $v - u = 0.486(3)$. The theoretical SC16 structure at AP has $u(\text{Ga}) = 0.1583$ and $v(\text{As}) = 0.6398$, and a calculated volume (per molecule) of 40.549 [14]. This volume equates to a lattice parameter of 6.871 Å, some $\sim 1\%$ smaller than that observed.

On pressure increase at RT, we observe no change until 22.0(7) GPa when the SC16 phase begins to transform to the *Cmcm* phase. This suggests a stability field of the order of 20 GPa, which is much larger than calculated by Mujica *et al.* [14]. However, the true equilibrium stability range of the SC16 phase is likely to be smaller than that suggested by the RT results, where large kinetic barriers almost certainly inhibit the phase transitions to the ZB and *Cmcm* phases. This is borne out by the present high-temperature results which show that SC16 is not the equilibrium phase above 14.5 GPa, nor below 13 GPa. This range of only ~ 1.5 GPa is closely similar to the 1.2 GPa calculated by Mujica *et al.* [14] suggesting that the true equilibrium range at RT is of this magnitude. The large difference from the experimental results at RT graphically illustrates the influence of kinetic effects in determining experimental transition pressures in this system.

The observation of both the SC16 and cinnabar structures means that GaAs is now unique among the III-V and II-VI semiconductors in having *two* strongly distorted tetrahedral phases at high pressure. It is interesting to compare their degrees of distortion. At 8.3 GPa, $a(\text{SC16}) = 6.739(2) \text{ \AA}$ [$V/V_0 = 0.847(1)$] and $u = 0.155(2)$ and $v = 0.642(2)$. At the same pressure, cinnabar-GaAs has $V/V_0 = 0.834(1)$ [19] and is thus 1.3(1)% denser than the SC16 phase. This greater density is accompanied by only a slightly greater distortion of the tetrahedra: SC16 has nearest-neighbor (nn) bondlengths of 2.369(19) and 2.426(19) \AA , while in cinnabar the bondlengths are 2.371(8) and 2.477(8) \AA [19,24]. But the nn bondangles in SC16 are $\sim 100^\circ$ and $\sim 118^\circ$, while in cinnabar they vary much more, from 91° to 141° [24]. In this sense cinnabar is the more distorted. However, since the distortion arises mostly from a simple twisting of the tetrahedra [25], cinnabar can also be seen as the less distorted. In any case, the existence of two quite differently distorted tetrahedral forms makes GaAs a particularly promising model system for studies of more complex and amorphous structures in binary materials.

In conclusion, we have found an SC16 phase of GaAs, the first observation of such a structure in a III-V semiconductor. The observation of SC16-GaAs realizes the earlier predictions of such a phase using *ab initio* calculations, and supports suggestions that the same structure may also be stable in other III-V systems [13,14,16]. The present results, along with the earlier determination of the SC16 structure in the copper halides, now invite experimental and computational study of the II-VI systems, where the more ionic bonding should facilitate the formation of SC16.

We acknowledge helpful discussions with G. J. Ackland and A. Mujica, and technical support from G. Bushnell-Wye and A. A. Neild. This work is supported by a grant from the Engineering and Physical Sciences Research Council, funding from the Council for the Central Laboratory of the Research Councils, and by facilities made

available by Daresbury Laboratory. M. I. M. acknowledges the support of a fellowship from the Royal Society.

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