Phase transitions in GaAs at high pressure and high temperature

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Introduction

GaAs is the prototype III–V semiconductor, and, as such, its high-pressure behavior has been the subject of considerable attention. On pressure increase at 300 K, GaAs has long been reported to transform from the ambient pressure zincblende (ZB) phase to an orthorhombic structure (space group Pmm2 at 17 Gpa), and then to a second orthorhombic structure (space group Imm2 at 24 Gpa) [1]. Using angle-dispersive (AD) diffraction techniques with monochromatic synchrotron radiation and an image plate area detector [2], we have recently restudied the high-pressure behavior of GaAs at the Synchrotron Radiation Source, Daresbury, UK. We have found: (i) that the Pmm2 and Imm2 structures are one and the same, and that the true structure has space group Cmcm [3]; (ii) that on pressure decrease at 300 K, the Cmcm structure transforms to a previously unobserved hexagonal structure before transforming back to ZB [4]; and (iii) that heating the Cmcm phase to above 423 K at ~15 GPa results in a transition to a second previously unobserved phase with the cubic SC16 structure (Figure 1), and that this structure is stable when the temperature is reduced back to ambient [5].

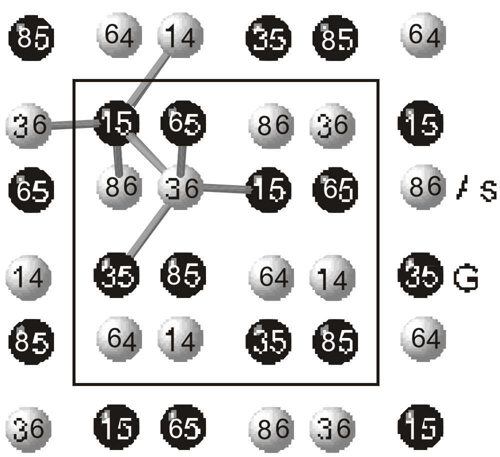

Figure 1: The SC16 structure of GaAs shown in projection down the z-axis. The numbers on each atom give the z coordinate in units of 0.01.

The SC16 structure (the binary equivalent of the metastable BC8 structure found in Si and Ge on pressure reduction from the high-pressure β–tin phase) has been the subject of recent *ab initio* calculations by Crain *et al.* [6] and Mujica *et al.* [7]. Both studies found SC16 to be an equilibrium phase of GaAs, with a calculated stability range of 1.2 GPa, from 11.5 GPa to 12.7 GPa [7]. Our AD studies suggested SC16 to be stable from 13 GPa to 14.5 GPa [5]. However, in our diffraction studies, we have observed transitions to the SC16 phase only from the Cmcm phase; neither we nor any previous worker has observed the ZB→SC16 transition upon pressure increase. A possible explanation for this was forwarded by Crain *et al.* [6], who suggested that the apparent absence of this transition upon pressure increase is because it is kinetically hindered at ambient temperature. They suggested, however, that the transition might occur at higher temperatures where such effects can be overcome.

Methods and Materials

While high-pressure, high-temperature (HP-HT) experiments can be conducted in a diamond-anvil cell, large-volume pressure cells, such as the T-cup, are ideally suited to such studies. We therefore conducted HP-HT experiments on GaAs using the T-cup cell on beamline 13-BM-D at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). The GaAs sample was a finely ground powder obtained from material of 99.9999% purity.

Results

Figure 2 shows the sequence of diffraction patterns collected on pressure increase at 400°C. At pressures up to 15.2 GPa, the diffraction patterns contain only ZB-phase sample peaks. However, on pressure increase to 16.1 GPa, peaks from the SC16 phase appear, as shown by the arrows in profile (d).

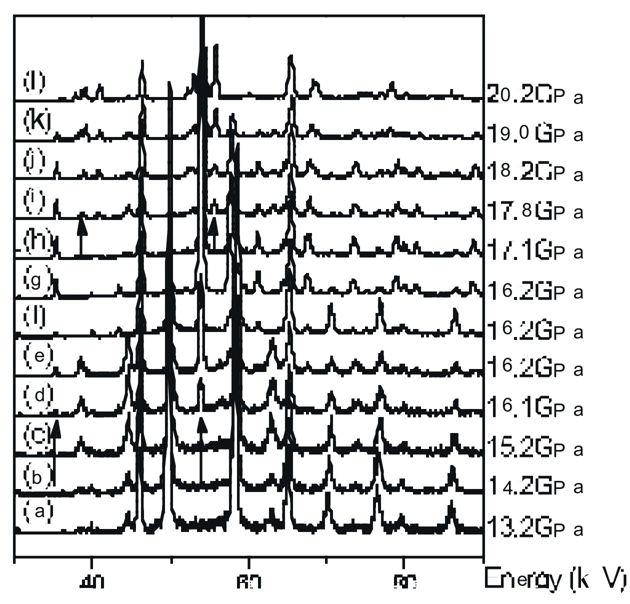

Figure 2: Diffraction profiles collected from GaAs on pressure increase at 400°C. The first appearance of the SC16 and Cmcm peaks is indicated in profiles (d) and (i), respectively.

The SC16-phase peaks increase in intensity with both time [profiles (e) to (g)] and increasing pressure, until, at 17.8 GPa, peaks from the Cmcm phase appear. At 20.2 GPa, only sample peaks from the Cmcm phase were observed.

On pressure decrease (Figure 3), no SC16 phase was observed until the pressure was decreased from 19.7 GPa (where no diffraction pattern was collected) to 17.4 GPa, as shown by the arrow in profile (b). The SC16 phase was stable until the pressure was decreased from 14.6 GPa to 13.8 GPa, at which point peaks from the ZB phase reappeared, as shown by the arrow in profile (f).

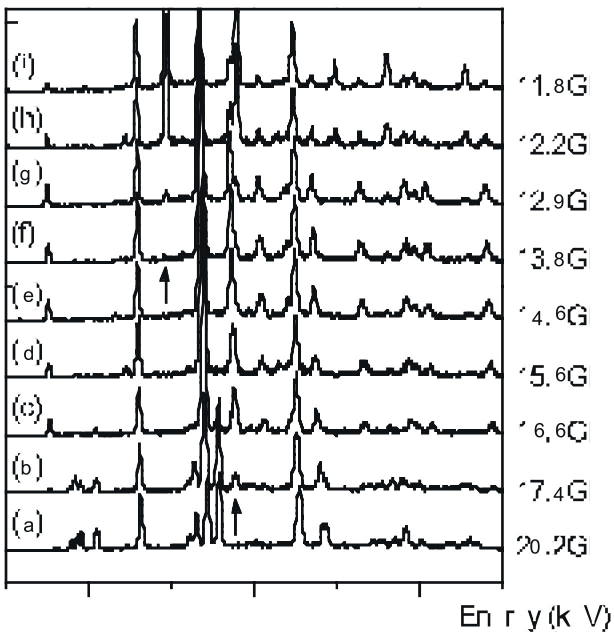

Figure 3: Diffraction profiles collected from GaAs upon pressure decrease at 400°C. The first appearance of the SC16 and ZB peaks is indicated in profiles (b) and (f), respectively.

Discussion

This is the first time that the ZB→SC16 transition has been observed in GaAs upon pressure increase, and the results confirm that this transition is almost certainly kinetically hindered at ambient temperature. Averaging the ZB→SC16 and SC16→ZB transition pressures of 15.7(5) GPa and 14.2(2) GPa, respectively, gives a ‘equilibrium’ transition pressure of 14.9 GPa for ZB→SC16, while the SC16→Cmcm and Cmcm→SC16 transition pressures of 17.5(4) GPa and 18.6(12) GPa, give an ‘equilibrium’ value of 18.0 GPa for the SC16→Cmcm transition. The stability range of SC16 is thus some 3.1 GPa, larger than both the theoretical value of 1.2 GPa [7], and our previous estimate of 1.5 GPa [5].

In the time available, we were able to complete only a single high-pressure run at 400°C. However, the confirmation of SC16 as an equilibrium phase enables very considerable doubts to be cast on the reported phase diagram of GaAs, which does not presently include SC16. Further extensive HP-HT measurements are thus now required, both to determine the true boundaries of the ZB, SC16, and Cmcm phases and to search for other high-pressure phases. The T-cup apparatus at APS is ideal for such future studies.

Acknowledgments

We would like to acknowledge the extremely helpful staff at ANL and APS who made our trip so successful. This work was supported by funds made available by the Engineering and Physical Sciences research Council and by the Royal Society. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38.

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