

Observation of a Cinnabar Phase in GaAs at High Pressure

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A previously unidentified high-pressure phase of GaAs has been found on pressure decrease from GaAs-II. The new phase is hexagonal, with a fourfold coordinated cinnabar structure very similar to that of ZnTe-II. The phase first appears on download from GaAs-II at 11.9(1) GPa, coexists with GaAs-I below 11.2(3) GPa, and starts to transform to GaAs-I at 8.1(2) GPa. Although no evidence of the phase is seen on pressure increase, detailed comparisons with ZnTe suggest cinnabar GaAs is an equilibrium phase. [S0031-9007(97)03052-4]

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Among the III-V semiconductors, GaAs has attracted the most attention in high-pressure studies. This interest has arisen because of the technological importance of GaAs, coupled with the facts that the high-pressure phases have appeared to be different from other III-V systems and yet have proved difficult to characterize definitively. The accepted phase transition sequence on pressure increase at room temperature (RT) in recent work has been GaAs-I (zinc blende) to GaAs-II (orthorhombic Pmm2) starting at ~ 17 GPa, GaAs-II to GaAs-III (orthorhombic Imm2) at 24(1) GPa, and GaAs-III to GaAs-IV (simple hexagonal) at 60–80 GPa [1]. However, new diffraction results using angle-dispersive techniques suggest that the true structure of GaAs-II is more complex, with space group Cmc \bar{m} [2,3], and this has been supported by the most recent computational studies [4,5]. The new diffraction studies also show that the structure above 24 GPa fits to Cmc \bar{m} too; there is no evidence of a transition from GaAs-II to a different phase III [3].

There has been equal interest recently in the structural behavior on pressure decrease. The generally accepted picture is that GaAs-II simply transforms back to the zinc blende phase, at ~ 10 GPa [6,7]. However, there have been several reports of other behavior. Venkateswaran *et al.* found evidence of a new phase in ambient-pressure optical spectra obtained from thin-film single-crystal samples decompressed from above 20 GPa [8]. In a preliminary account of their studies, Besson *et al.* reported features in their Raman spectra on pressure decrease which they attributed to a new phase at ~ 10 GPa [9], though they later ruled out this interpretation in favor of vacancy defect effects [7]. And Tsuji *et al.* [10] observed additional diffraction peaks appearing at ~ 11 GPa on pressure decrease from 25 GPa; unlike Venkateswaran *et al.* [8], they found complete transformation of the sample back to the zinc blende phase by ~ 5 GPa [10].

In this Letter we report a detailed study of GaAs on both pressure increase and decrease at RT using angle-dispersive diffraction techniques. We find a new hexagonal phase between the GaAs-II (Cmc \bar{m}) and zinc blende (ZB) phases on pressure decrease, with a fourfold coordinated cinnabar structure that is very similar to that reported

previously for ZnTe-II [11]. The existence of this phase raises questions as to the true transition sequence.

Diffraction data were collected at room temperature on station 9.1 at the Synchrotron Radiation Source, Daresbury, using an image-plate area detector [12]. The incident wavelength was 0.4447 Å. Finely ground samples were made from starting material of 99.999% purity supplied by the Aldrich Chemical Company and were loaded with 4:1 methanol:ethanol as a pressure transmitting medium and chips of ruby for pressure measurement.

On pressure increase, the transition from ZB to Cmc \bar{m} was first observed at 17.3(2) GPa, and was not complete until 23.4(4) GPa, in good agreement with previous studies [1,7]. On pressure decrease, new peaks appeared in the diffraction profiles at 11.9(1) GPa that are not consistent with the ZB structure, such as the one marked by the arrow in Fig. 1(a). On further pressure decrease, these new peaks increased in intensity. At 11.2(3) GPa, however, peaks consistent with ZB also appeared in the diffraction profile, as indicated by the arrow in the 11 GPa profile of Fig. 1(b). Further reductions in pressure increased the intensity of both phases at the expense of the peaks from Cmc \bar{m} —Fig. 1(c). At 8.3(2) GPa, only peaks from the new phase and ZB remained in the profile, as illustrated in profile (d) of Fig. 1. Further reductions in pressure resulted in a transition from the new phase to ZB, and below ~ 4 GPa only broadened peaks from ZB remained.

It has not proved possible to obtain single-phase samples of the new phase, and so structure solution had to be carried out on mixed-phase profiles. After subtraction of the best fitting ZB profile from the pattern in Fig. 1(d), the diffraction pattern from the new phase was found to bear a striking resemblance to that of ZnTe-II, which we have previously reported as having a hexagonal cinnabar structure [11]. We found that the same structure—space group P3 $_1$ 21, with atoms on the 3(a) and 3(b) sites at $(u, 0, 1/3)$ and $(v, 0, 5/6)$, respectively, and $u \approx v \approx 1/2$ —gave an excellent fit. Figure 2 shows a ZB/cinnabar fit to the diffraction pattern in Fig. 1(d), using the Rietveld refinement program MPROF [13]. The refined lattice parameters are $a = 5.474(1)$ Å for ZB [$V/V_0 = 0.908(1)$] and $a = 3.883(1)$ Å, $c = 8.657(2)$ Å

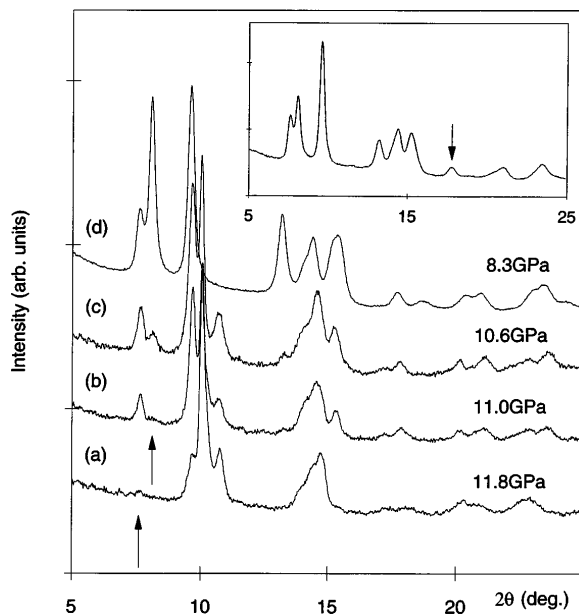


FIG. 1. Integrated profiles of the patterns recorded from GaAs on pressure decrease at (a) 11.8 GPa, (b) 11.0 GPa, (c) 10.6 GPa, and (d) 8.3 GPa. The arrows in profiles (a) and (b) mark the first appearance of a peak from (a) the new phase, and (b) the zinc blende phase. The inset shows an integrated profile recorded from a different sample at 8.2 GPa; the arrow marks the cinnabar (114)/(006) doublet (see Fig. 2).

for cinnabar [$V/V_0 = 0.834(1)$]. From extrapolation, the relative volume of Cmcm at the same pressure is $V/V_0 = 0.765(2)$ [3]. Cinnabar GaAs at 8.3 GPa is thus some 7.4% denser than ZB, and 6.9% less dense than Cmcm.

The refinements show that the sample contains 32(1)% of the cinnabar phase. This phase was found to be

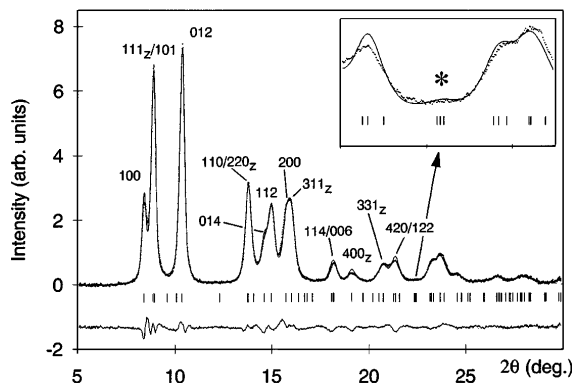


FIG. 2. Rietveld refinement fit to the mixed-phase profile in Fig. 1(d). The tick marks show the positions of all the reflections allowed by symmetry. The difference between the observed and calculated profiles is displayed below the tick marks. The strongest low-angle reflections are indexed, and the subscript z denotes a peak from the zinc blende (ZB) phase. Indices separated by an oblique line denote overlapping reflections; an example of a cinnabar phase reflection with $l = \text{odd}$, (101), overlapped by a ZB reflection, (111), is shown. The inset enlarges the region around the (213)/(107)/(116) triplet, marked by an asterisk.

quite strongly affected by preferred orientation, which was accounted for in the calculated profile by the standard March-Dollase model in MPROF [13]. A second preferred-orientation parameter was refined to model a smaller effect in the ZB phase. The profile in the inset in Fig. 1 shows an example of a different mixed-phase sample (at 8.2 GPa) with 41(1)% of the cinnabar phase and greater preferred orientation in the ZB phase—such that the (400) ZB reflection at $2\theta = 18.7^\circ$ in profile (d) becomes too weak to detect.

The refined atomic coordinates for the cinnabar phase at 8.3 GPa are $u(\text{Ga}) = 0.539(2)$ and $v(\text{As}) = 0.505(2)$. These are very different from those observed previously in the cinnabar phases of CdTe [14] and the Hg chalcogenides [15]—where $u \sim 0.7\text{--}0.6$ and $v \sim 0.56$ —but are exactly the same as those obtained for ZnTe-II, where $u = 0.540(2)$ and $v = 0.504(2)$ at 8.9 GPa [11]. The c/a ratio of 2.229(1) is also close to the value of 2.289(1) in ZnTe-II [11]. The resulting coordination of cinnabar GaAs is thus like that of ZnTe-II in being close to fourfold, rather than the $2 + 4$ or $4 + 2$ coordinations in the other known cinnabar structures [14,15]. The nearest-neighbor (nn) bond lengths in cinnabar GaAs at 8.3 GPa are two at 2.371(8) Å and two at 2.477(8) Å. This compares with four nn bond lengths of 2.370(1) Å in GaAs-I at the same pressure. The next nearest neighbors in cinnabar GaAs are considerably farther away, with 14 atoms in the range 3.48–3.88 Å, compared with 12 atoms at a distance of 3.871(1) Å in GaAs-I.

The analysis and description of cinnabar GaAs so far has been in terms of a site-ordered structure. In our studies of other cinnabar phases [11,14,15], we were able to show this ordering directly by observing the weak (003) reflection, the intensity of which depends only on the difference in scattering power of the constituent atoms. But because of the similar scattering power of Ga and As and the broadening of the diffraction peaks, this reflection is too weak to detect in our GaAs diffraction profiles. We are thus unable to determine whether the structure is long-range site ordered or not.

If the structure were site disordered (and thus quasis-monatomic), and $u = v$, then *all* reflections with $l = \text{odd}$ would be absent; the unit cell would be halved along c and the structure would be the same as that of Se or Te at ambient pressure. For the refined (nonequal) values of u and v there are only six reflections with $l = \text{odd}$ having intensities large enough to be observed. Unfortunately, the strongest of these are all overlapped by ZB reflections (see Fig. 2), and the (213)/(107) doublet is overlapped by the 4 times stronger (116) reflection in the weak triplet marked by an asterisk in the inset of Fig. 2. Nonetheless, simulations show that the difference between u and v — Δx —can be no larger than the 0.03–0.04 obtained from the fit shown in Fig. 2; at Δx values significantly higher than this, the calculated intensity of the (213)/(107)/(116) triplet peak becomes clearly larger than is observed. Because of the problems of peak overlap, we cannot put a

confident *lower* bound on Δx . Though we cannot then completely rule out the possibility that u and v are the same, a refinement of the 8.3 GPa profile of Fig. 1 with them constrained to be equal gives a significantly poorer fit than the free refinement with $u = v = 0.525(1)$. The further possibility that $u = v$ and the structure is randomly site disordered such that it is Se-like—with three 50:50 Ga/As “atoms” per unit cell—seems improbable on energy grounds.

In addition, though we cannot distinguish the Ga and As atoms, the remarkable similarity of the freely refined atomic coordinates to those of ZnTe-II (see above) strongly favors site ordering and the proposed allocation of sites—with Ga displaced from an x coordinate of 0.5 by more than As, as for Zn and Te in ZnTe-II. There is no doubt about the site allocation in ZnTe-II [11], and this gives a structure in which the Te-Zn-Te angle (141°) is larger than the Zn-Te-Zn angle (127°) in the spiral chains formed by the two shortest nn bonds. This difference in the nn-chain angles at the metal and the chalcogen is a feature of all cinnabar structures studied to date [15], and reflects the relationship to the NaCl structure, in which these angles are 180° and 90° , respectively [15]. The cinnabar GaAs structure in this configuration has As-Ga-As and Ga-As-Ga angles of 140° and 127° , respectively. The fact that this distinction between the two sites emerges in the freely refined structure makes it likely that there is site ordering, at least on a short length scale. Whether or not that is so, the GaAs and ZnTe cinnabar structures are clearly very alike, and quite different from the other cinnabar structures, in all of which the third-nearest neighbors are much closer and the nn-chain angles at the metal and chalcogen are much nearer to the ideal NaCl values, at about 170° and 105° [14,15].

We have made a detailed study of the transitions between the cinnabar, ZB, and Cmc m phases, and the pressure ranges over which the transitions occur. As noted previously, the ZB \rightarrow Cmc m transition takes place from 17.3(2) to 23.4(4) GPa, while the reverse transition takes place from 11.2(3) GPa to 8.3(2) GPa. On pressure decrease, the Cmc m \rightarrow cinnabar transition starts at 11.9(1) GPa, as already noted, and ends at 10.3(3) GPa—determined as the pressure at which the intensities of the cinnabar peaks cease to change. By repressurizing a two-phase ZB/cinnabar sample made at ~ 8 GPa, the cinnabar \rightarrow Cmc m transition was found to take place from 15.1(2) GPa, as determined by the first appearance of Cmc m peaks, to 19.4(5) GPa, at which pressure the cinnabar peaks had disappeared. Finally, a Cmc m -free sample made at ~ 8 GPa and then repressurized to 11 GPa was used to locate the cinnabar \rightarrow ZB transition. From the intensities of the cinnabar and ZB peaks on pressure decrease from 11 GPa, the range of the transition was determined as 8.1(2) GPa, where the cinnabar peaks began to decrease in intensity, to 3.9(3) GPa, where they had disappeared. These transition pressures and ranges of coexistence are illustrated schematically in Fig. 3.

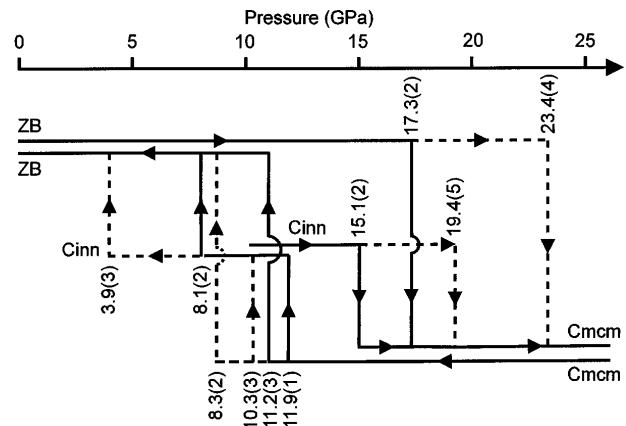


FIG. 3. Schematic representation of the phase transitions between the zinc blende (ZB), cinnabar, and Cmc m phases of GaAs on pressure increase and decrease. Solid vertical lines mark the onset of transitions while dashed lines indicate the ranges of coexistence, at the pressures shown.

What light does this all throw on the various previous results obtained on pressure decrease? The diffraction pattern identified by Vohra *et al.* [6] as a mixture of GaAs-III and ZB at 9.4 GPa [their Fig. 4(b)] is, in fact, remarkably similar to the pattern in the inset to our Fig. 1. In particular, the peak at 25.1 keV in their data is in the wrong place to be the (400) reflection from ZB—or a GaAs-III reflection. But it fits very well as the cinnabar (114)/(006) doublet indexed in Fig. 2 and marked by an arrow in the Fig. 1 inset. Also, the pressure range over which Vohra *et al.* [6] detect the transition from GaAs-II—in reflectivity measurements—is from 12 to 9 GPa, in good agreement with our results (we see only residual Cmc m below ~ 9 GPa). Tsuji *et al.* [10] also detect the transition from Cmc m to ZB plus a new phase over a very similar range—from 11.5 to 9 GPa. They reported just two diffraction peaks from the new phase: a weak one at a d spacing of 3.30 Å and a stronger one at a d spacing of 2.69 Å at 10 GPa. These are close to the positions of the two strongest nonoverlapped cinnabar reflections, (100) and (012), which we observe at $d = 3.336$ and 2.640 Å, respectively, at 10.4 GPa. The fact that the new phase reported by Venkateswaran *et al.* [8] exists at ambient pressure indicates clearly different behavior. In addition, the new phase is found only on pressure decrease from above 20 GPa, whereas we find no difference between samples taken to 18–19 GPa and to 25 GPa. No information is given about the transition pressure to the new phase—results are shown only at ambient pressure—so no comparison with other studies can be made on that basis. However, the authors argue that the new phase is more likely to be a distortion of the high-pressure NaCl-like forms rather than a distortion of ZB, and hence speculate that cinnabar could be a candidate; they show that the agreement with the calculated spectrum of HgS cinnabar is plausible if rather approximate. (An imperfect fit is unsurprising in view of the differences now revealed between the HgS and GaAs cinnabar

structures.) Moreover, the two decisively non-ZB peaks in the data of Venkateswaran *et al.* are very similar to the non-ZB features reported in Raman spectra on pressure decrease by Besson *et al.*—appearing at ~ 10 GPa [7]. As already noted, Besson *et al.* first attributed these features to a new phase [9], but later offered the different interpretation that they are caused by defects, most probably in the form of transition-induced As vacancies [7]. But in their extended x-ray absorption fine structure (EXAFS) data on pressure decrease, Besson *et al.* observe significantly nonfourfold coordination down to 5 GPa [7]. This is well below the minimum pressure at which we have detected Cmc \bar{m} (≥ 8 GPa), and is a clear signature of the cinnabar phase. (Although the cinnabar coordination is quasifourfold, the difference of 0.1 Å between the first two and the next two nearest neighbors is an easily detectable departure from ZB coordination in the EXAFS measurements.) If that conclusion is coupled with the fact that the new features in the Raman spectra first become readily detectable around 10 GPa, and almost disappear “a few gigapascals above ambient” [7]—in keeping with the pressure range shown in Fig. 3—it seems probable that these features arise from the cinnabar phase rather than defects. Combined Raman and diffraction studies would be needed to be sure of this. In the meantime, the balance of evidence suggests that Venkateswaran *et al.* [8] also observed the cinnabar phase, but with significantly different ranges of stability perhaps caused by the thin-film nature of their samples.

It thus emerges that the cinnabar phase of GaAs has almost certainly been observed before on pressure decrease, with the same transition pressures as we now report, by Vohra *et al.* [6], Tsuji *et al.* [10], and Besson *et al.* [7], but not identified as such—and probably also by Venkateswaran *et al.* [8]. The observation by Vohra *et al.* [6] that there is no further increase in reflectivity below 9 GPa suggests that this phase is semiconducting, and, if Venkateswaran *et al.* [8] did indeed have the same phase, then their opacity observations indicate that the cinnabar band gap is below 1.5 eV at ambient pressure. (ZnTe-II is also semiconducting, but with a band gap of ~ 2.5 eV at 10 GPa [16].)

We observe no evidence in this study of a ZB \rightarrow cinnabar transition in GaAs on pressure increase, suggesting, perhaps, that the cinnabar phase is not a true equilibrium phase. However, in a system which exhibits such large hysteresis and wide ranges of phase coexistence, it is extremely difficult to determine true thermodynamic stability. In fact, the remarkably close similarities in the structures and behavior of GaAs and ZnTe strongly suggest that cinnabar *is* a true equilibrium phase of GaAs. On pressure increase, ZnTe undergoes a ZB \rightarrow cinnabar transition at ~ 9 GPa, and a cinnabar \rightarrow Cmc \bar{m} transition at ~ 11 GPa [12,17]. As shown, the cinnabar structures are very similar in both materials. A comparison of the Cmc \bar{m} structures reveals that these, too, are very alike in the degree of distortion of both their unit cells

and their coordinates from the NaCl structure [3,17]. In ZnTe, there is little doubt that cinnabar is a true equilibrium phase as it is observed on both pressure increase and decrease. It therefore seems very probable that cinnabar GaAs, too, is an equilibrium phase, but that the ZB \rightarrow cinnabar transition—which is between two quite different fourfold coordinated structures—is too kinetically hindered at room temperature to occur before the sample transforms to Cmc \bar{m} .

The probable existence of a previously unrecognized equilibrium phase between GaAs-I and GaAs-II requires a reassessment of the much studied transition to GaAs-II, including further experimental investigations. The close similarity in behavior between GaAs and ZnTe adds to the growing links in structural systematics between the III-V and II-VI semiconductors [3]. It would now be particularly interesting to explore the relationship between GaAs and ZnTe further by searching for the equivalent of the Cmc \bar{m} \rightarrow NaCl transition observed in ZnTe at high temperature [18].

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