

Stability and electronic structure of the cinnabar phase in GaAs

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We have performed *ab initio* pseudopotential calculations to investigate the pressure-induced phase transitions in GaAs in the light of the recent experimental observation of a stable cinnabar structure. We find that a cinnabar structure is metastable with respect to other candidate structures, although extremely close to stability for pressures in the region of 16 GPa. This is in good agreement with experiment, where it has been observed to coexist with the zinc-blende and *Cmcm* phases in this pressure regime. It had been suggested that the cinnabar structure is the only known semiconducting high-pressure phase in a III-V compound. We perform band-structure calculations on this high-pressure structure and confirm that the material is semiconducting. [S0163-1829(98)51104-6]

I. INTRODUCTION

The structural phase transitions in gallium arsenide have been an area of intensive study for a number of years. Despite this continued interest there has never been complete agreement between experiment and theory on the nature and relative stability of high-pressure structures. Early work appeared to show on the existence of a high-pressure metallic phase probably an orthorhombic distortion of β -Sn, but more recently, *ab initio* pseudopotential calculations^{1,2} predicted that the first transition from the ambient pressure zinc-blende structure should be to a distorted tetrahedral structure (SC16). More accurate x-ray diffraction experiments using image plate techniques showed discrepancies with earlier work. It found subtle peaks in the high-pressure diffraction pattern that identified that the β -Sn phase was in fact a *Cmcm* structure.³ However, results of a theoretical study⁴ were not able to confirm the stability of *Cmcm* over β -Sn, and a predicted region of SC16 stability remained.

Further experimental studies on pressure decrease by Tsuji *et al.*⁵ reported observing two extra peaks in the diffraction pattern for GaAs at 10 GPa, which were ascribed to an unknown metastable phase. These are in fact consistent with the calculated SC16 structure¹ and the cinnabar structure⁶ but were insufficient for a full structural solution.

Very recently, McMahon and Nelmes⁶ have obtained clearer evidence of the nature of the phase between zinc blende and *Cmcm*. They showed that this phase possesses hexagonal symmetry and is remarkably similar to the reported cinnabar phase in ZnTe. Like the ZnTe cinnabar phase the GaAs phase is a four-fold coordinated structure. This is unlike the cinnabar phases reported in the other II-VI materials, HgS and HgSe, which report a six-fold coordination. McMahon and Nelmes also report the sequence of transitions as being zinc blende to *Cmcm* directly with no intermediate phase on increasing pressure. However, a cinnabar phase is observed on the downstroke indicating an easier transition route from *Cmcm* to cinnabar than to zinc blende. Once the cinnabar phase is formed it persists on increasing pressure before transforming to *Cmcm* at around 15 GPa. A summary of the experimental findings is shown in Fig. 1. Furthermore, with hindsight one can see evidence in other earlier work⁷⁻⁹ of this cinnabar phase. If this is indeed the case, then the reflectivity measurements⁷ suggest cinnabar

should be nonmetallic while the observed opacity^{8,10} suggests a small band gap.

The structure is more closely related to *Cmcm* than zinc blende is, thus we expect the kinetics to favor the *Cmcm*-cinnabar transition over the *Cmcm*-zinc blende allowing cinnabar to form on depressurization.

However, the transition from zinc blende to either *Cmcm* or cinnabar faces similar kinetic barriers, being a massive reconstructive transition. Thus one would not expect to see the metastable cinnabar phase on the upstroke.

In this paper, we report first-principles density functional theory (DFT) pseudopotential calculations of the cinnabar phase and compare its stability to other candidate structures likely to be formed in high-pressure experiments. We also demonstrate that it is a small band-gap semiconductor that is very close to stability in the pressure range about 16 GPa.

II. METHODOLOGY

We have used the first-principles pseudopotential method within the density-functional formalism, which is well docu-

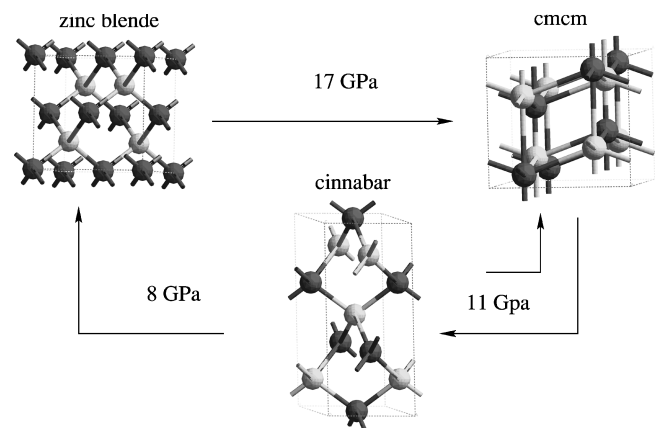


FIG. 1. Zinc blende transforms to *Cmcm* starting at around 17 GPa. On depressurization at around 11 GPa the cinnabar structure is first observed, before returning to zinc blende at around 8 GPa. If the cinnabar phase is pressurized then the sample returns to *Cmcm*. Some of the *Cmcm* appears to transform directly to zinc blende, and coexistence of all three phases is seen at intermediate pressure.

mented elsewhere.¹¹ This method replaces the strong ionic core with a weaker pseudopotential with the same scattering behavior, the pseudo-wave-functions are then expanded by plane-wave basis functions. The basis set was truncated at an energy of 250 eV, which converged total energy differences to better than 0.1 meV/atom. The use of a plane-wave basis set simplifies the calculations since there are no Pulay forces¹² arising from changes in the basis set to be considered. Kleinman-Bylander norm-conserving pseudopotentials¹³ were used and the local-density approximation (LDA) to exchange and correlation was employed using the Perdew-Zunger¹⁴ parameterization to the Ceperley-Alder¹⁵ form. Electronic relaxation was performed using a preconditioned conjugate gradients scheme. Forces on atoms were calculated using the Hellmann-Feynman theorem, which allows optimization of the atomic positions. Ionic relaxation was then performed also using a conjugate gradient method.

Reciprocal space integration was done by k -point sampling with sets of special points obtained by the Monkhorst-Pack¹⁶ (MP) method. For the semiconducting zinc-blende phase we have used a $6 \times 6 \times 6$ MP set, for the SC16 phase a $4 \times 4 \times 4$ MP set was used, and for the metallic β -Sn and $Cmcm$ phases $14 \times 14 \times 14$ and $12 \times 12 \times 12$ MP sets were used, respectively. For the cinnabar phase a $7 \times 7 \times 3$ MP set was used. These were sufficient to converge the total energies to at least 3 meV per atom for all structures considered.

III. STRUCTURE

We have calculated the total energy of the zinc-blende, $Cmcm$, cinnabar, SC16, R16, and β -Sn structures as a function of volume. The R16 structure is the diatomic equivalent of the R8 structure found to be stable in silicon, which is formed from depressurization from the metallic phase.¹⁷ Although it forms an important part of the transition route between the high-pressure metallic phase and the ambient pressure metastable BC8 phase in the monoatomic case, it is unlikely to exist in GaAs due to the odd-membered rings in the structure, which therefore require like-species bonding. It is unlikely that the tetragonal and orthorhombic structures compress uniformly with pressure. Therefore, we optimize each unit-cell parameter as a function of pressure in those cases. In Fig. 2 the total energy per formula unit (GaAs pair) against volume for the phases considered here are plotted. The lines are fits to the Murnaghan equation of state for the points. Also plotted, in Fig. 3, is the enthalpy differences versus pressure for the structures considered.

The cinnabar structure can be seen in Fig. 1. Our calculated cinnabar structure has $a=3.883$ Å and $c=8.551$ Å at the minimum of its curve (zero pressure), however, the transformation back to zinc blende will have occurred before that point could be reached. In its regime of stability around 16 GPa, cinnabar has lattice constants $a=3.693(1)$ and $c=8.1316(1)$ Å. We allow the free internal parameter of the cinnabar structure to relax but find that it is unaffected by pressure, being $u=0.5000(1)$ for both Ga and As at all volumes considered here. The experimental values are $a=3.883$ and $c=8.657$ Å at 8.3 GPa,⁶ so the agreement with high-pressure x-ray diffraction experiments is good; at 8.3 GPa we differ by only $\sim 2\%$. The experimental free parameters are

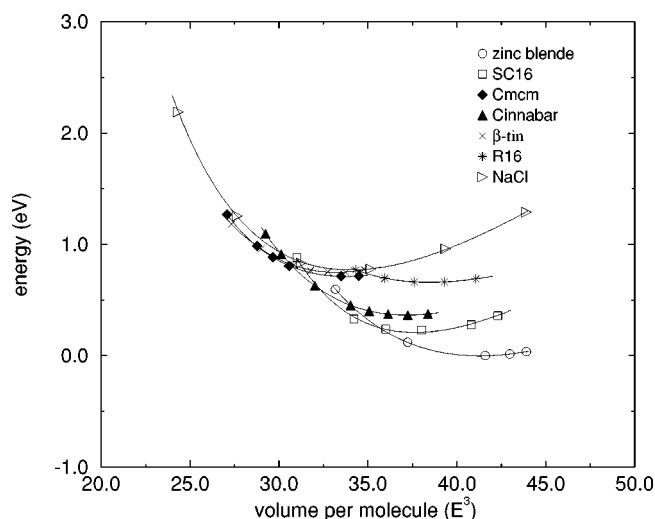


FIG. 2. Graph showing energy vs volume for various phases of GaAs. Circles are the zinc blende phase, squares are SC16, triangles are cinnabar, diamonds are $Cmcm$, crosses are β -Sn, and stars are R16. Ignoring the kinetically inaccessible SC16 structure, the common tangent between zinc blende and $Cmcm$ is slightly below the cinnabar curve, but the difference is within the error of the calculation.

0.539 for Ga and 0.505 for As. There is no qualitative difference between our theoretical predictions and the experiment—both are fourfold coordinated systems.

The $Cmcm$ structure is shown in Fig. 1. It contains four atoms in the orthorhombic cell, having three independent lattice parameters, a , b , and c and two free internal parameters; one for each species corresponding to motion in the z direction of the primitive cell. We allow all five of these parameters to vary with pressure. A full description of the structure is given in Ref. 4. Our calculated $Cmcm$ structure has an equilibrium volume of 33.48 Å³ per molecule with $c/a=1.049$ (experimental 1.055) and $b/a=0.952$ (experimental 0.973) similar to Ref. 4.

The (negative of the) gradient of the tangent between pairs of energy-volume curves gives the transition pressure

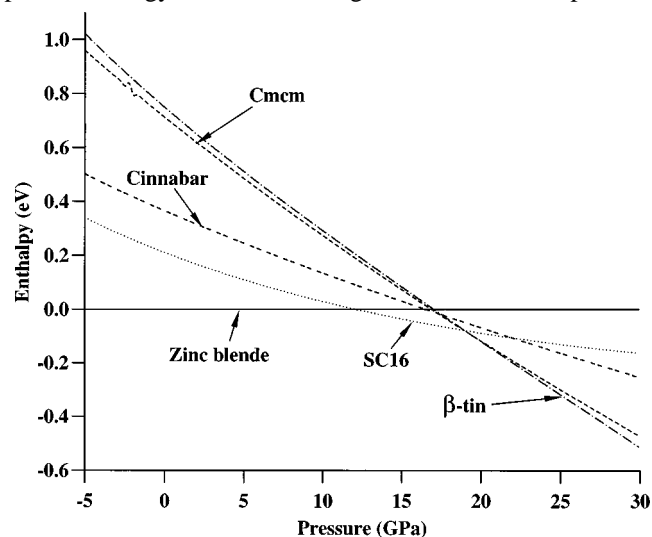


FIG. 3. Graph showing enthalpy relative to zinc blende against pressure for all of the structures studied except R16. The predicted transition sequence is zinc blende to SC16, then to $Cmcm$ before going to β -Sn.

between those two phases. This only takes energy differences into account and cannot give any insight as to the ease of the transition kinetics and will therefore tend to underestimate observed upstroke transition pressures. The calculated zinc-blende to *Cmcm* transition pressure is 16.4 GPa. As expected, this is slightly lower than the experimentally observed value (17.3 GPa). The pressure for the zinc-blende to cinnabar transition is, to within the error of the calculation, the same; i.e., we predict a value of 16.4 GPa for the cinnabar to *Cmcm* transition that is good agreement with McMahon and Nelmes,⁶ who find that this transition starts at approximately 15 GPa and is complete by 19 GPa.

It has been predicted in previous work¹ and here that the SC16 structure is the stable phase around 13 GPa. The SC16 phase is the binary equivalent of the BC8 phase² found in silicon on depressurization. It has a cubic structure with two free parameters, one for each species. Our relaxed structure has a lattice constant of 6.75 Å and the free parameters are 0.095 and 0.107 for Ga and As, respectively. This is in good agreement with previously reported values.^{2,4} A full description of the SC16 structure can be found in Ref. 2.

As expected, we find that the intermediate R16 structure is extremely unfavorable with respect to other intermediate phases. Its equation of state lies approximately 0.4 eV/atomic pair (approximately 2000 K) above the SC16 structure. Thus the intermediate phase found in silicon between metallic and BC8 structures is absent in GaAs, and the transition kinetics into SC16 are consequently more difficult.

The stability of SC16 was ascribed to its ability to maintain fourfold-coordinated covalent bonding with relatively small distortion from the tetrahedral angle, while reducing the volume per atom. Cinnabar achieves a similar result, with the tetrahedral angles distorting away from the perfect tetrahedral angle of 109.6 to 106.8 and 110.8.

We have also investigated the electronic structure of the cinnabar phase. We have calculated the band structure for the equilibrium structure, which is shown in Fig. 4. It is found that the cinnabar phase is semiconducting with an indirect band gap between the Γ point in the valence band and the *M* point of the conduction band of 0.26 eV at 16 GPa. The unstable zero-pressure cinnabar structure is also semiconducting with a direct band gap at Γ of 0.09 eV. It is well known that DFT LDA underestimates band gaps, therefore we expect the gap to be slightly larger than this. In our calculations, we make the assumption that the closed *d* shell of electrons in the Ga is fully described as core electrons in the pseudopotential. In the atomic case, we find that the *d* electrons lie significantly lower in energy than our assumed valence electrons (Ga $4s^24p^1$ and As $4s^24p^3$). Some calculations⁴ have been performed that make some attempt to include the effects of the *d* electrons via nonlinear core corrections find a slightly reduced region of SC16 stability.

To summarize, it was previously thought that the β -Sn structure was the first high-pressure metallic phase of GaAs.

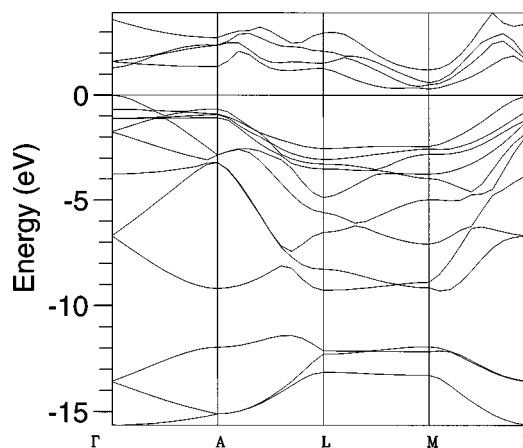


FIG. 4. The band structure of the cinnabar phase GaAs at 16 GPa. There exists an indirect band gap of 0.26 eV. The Fermi level is at the zero of energy.

However, recent accurate experimental³ studies show that this phase in fact has the *Cmcm* structure. Other recent calculations⁴ show that the β -Sn and *Cmcm* structures are extremely close in energy, with the β -Sn structure being favored beyond a transition pressure slightly larger than 12 GPa. We also find the structures to be very similar in total energy, with the *Cmcm* phase being favored at lower pressures, in agreement with experiment. In both cases the difference in *Cmcm*– β -Sn energy is within the expected error of the calculation.

IV. DISCUSSION

The equation of state of the cinnabar phase in GaAs has been calculated. It is found to be extremely close to being a stable phase at 16.4 GPa. This is consistent with recent experimental observation, in which it was observed on depressurization from the *Cmcm* phase but not on increasing pressure from the diamond phase.

This behavior is consistent with easy phase transition kinetics between *Cmcm* and cinnabar, but slow kinetics between zinc blende and either phase.

Moreover, we have been able to confirm speculation that this is a small-band-gap semiconducting phase. This is unique among observed high pressure phases in III-V compounds (other than nitrides), which are otherwise metallic.

One discrepancy with experiment remains, the prediction that SC16 should have a region of stability and hence that cinnabar is not an equilibrium phase. This can be understood if formation of SC16 is kinetically hindered, which is extremely likely given the high energy of the intermediate R16 structure. In this case, as is suggested by Refs. 2 and 1, SC16 may be formed under conditions of high pressure and temperature and could then persist as a metastable state to ambient pressure.

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