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LETTER TO THE EDITOR

## The *Cmcm* structure as a stable phase of binary compounds: application to GaAs-II

Andrés Mujica† and R J Needs‡

† Departamento de Física Fundamental y Experimental, Universidad de La Laguna, La Laguna E-38205, Tenerife, Spain

‡ Theory of Condensed Matter Group, Cavendish Laboratory, University of Cambridge, Cambridge CB3 0HE, UK

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**Abstract.** We have studied the orthorhombic high-pressure phase II of GaAs. We find that the structure previously suggested for this phase is unstable and leads to the same *Cmcm* structure which was recently found in high-pressure studies of ZnTe and CdTe. We have investigated the mechanism for the distortion leading to *Cmcm*. Our calculations show that *Cmcm* GaAs becomes thermodynamically stable at 120 kbar in agreement with experimental data for GaAs-II. The available experimental structural parameters are consistent with this *Cmcm* structure, which may be common among II–VI and III–V compounds.

Recent developments in angle-dispersive powder x-ray diffraction techniques have led to the determination of complex structures in the high-pressure phases of several III–V and II–VI compounds [1–3]. In the light of the new findings for related materials it is interesting to reconsider the structure of the high-pressure phases of GaAs.

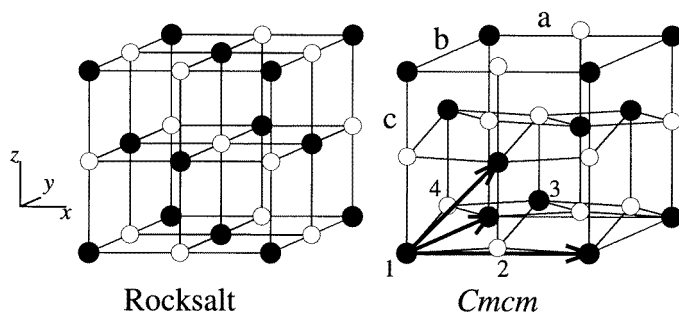
Despite the large number of experimental studies of GaAs, some features of its high-pressure phase diagram remain clouded. At a pressure of about  $120 \pm 15$  kbar GaAs undergoes a structural transition from the zinc-blende phase (GaAs-I) to a new phase (GaAs-II) of orthorhombic symmetry [4]. On further pressure increase several changes in the diffraction pattern of phase II occur, suggesting further structural transitions to the orthorhombic phases labelled III and IV [5].

Initially the high-pressure phase II was believed to consist of a mixture of the  $\beta$ -tin and rocksalt phases, and indeed early calculations [6] found the  $\beta$ -tin and rocksalt structures to be close in enthalpy and thermodynamically favoured over the other structures considered in the relevant pressure range. Further experimental work on GaAs-II [5] suggested an orthorhombic structure with atomic sites at  $(0, 0, 0)$  and  $(0, \frac{1}{2}, u)$ ,  $u \approx 0.35$ , (space group *Pmm2*) although the similarity in the atomic form factors of Ga and As precluded the determination of the ordering of the atoms on the lattice. Following this suggestion, Zhang and Cohen [7] performed a first-principles calculation at a single volume for a structure with four atoms per unit cell which corresponds to a certain ordering of the atomic species on the lattice of sites suggested by experiments. They found this structure to be thermodynamically favoured over the rocksalt structure, with lattice constants in reasonable agreement with the reported experimental values.

In this paper we study the stability and structure of GaAs-II. Our calculations show that the structure proposed for GaAs-II in [7] *cannot* be stable in a binary compound such as GaAs. The instability leads to a structure of space group *Cmcm* which is more stable than all the other phases considered in the pressure range in which GaAs-II is observed, and

we propose that this  $Cmcm$  phase is GaAs-II. The available experimental observations are consistent with this structure. The  $Cmcm$  structure includes as a special case the rocksalt structure which has been observed as a high-pressure phase in several III-V, II-VI and I-VII compounds. Moreover, this structure has recently been identified as the high-pressure phase III of ZnTe [2], and as a high-pressure phase of CdTe [3] and it is probably common among II-VI and III-V compounds at high pressure. To our knowledge this is the first theoretical study of such a structure in any compound [8].

The structure previously proposed for GaAs-II [7] can be constructed by a distortion of the rocksalt structure consisting of an orthorhombic adjustment of the axes and the shearing of alternate (010) planes in the [001] direction. There are two Ga-As pairs per unit cell. The structure is defined by the three lattice constants  $a$ ,  $b$  and  $c$ , and the internal parameter  $u$ , which corresponds to the relative displacement of the alternate (010) planes. In units of the three lattice constants the translation vectors are  $\mathbf{a}_1 = (1, 0, 0)$ ,  $\mathbf{a}_2 = (0, 1, 0)$ ,  $\mathbf{a}_3 = (\frac{1}{2}, 0, \frac{1}{2})$ , and the atomic sites of the four atoms in the unit cell are  $\tau_1^1 = (-\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}u)$ ,  $\tau_2^1 = (\frac{1}{4}, \frac{1}{4}, \frac{1}{4}u)$  (for atoms of species 1) and  $\tau_1^2 = (\frac{1}{4}, -\frac{1}{4}, -\frac{1}{4}u)$ ,  $\tau_2^2 = (-\frac{1}{4}, \frac{1}{4}, \frac{1}{4}u)$  (for atoms of species 2). This structure corresponds to a particular ordering of the atomic species on the lattice of sites of  $Pmm2$ , which effectively doubles its unit cell. However, this ordering leads to a further distortion of the lattice giving the  $Cmcm$  structure, as will be shown below.



**Figure 1.** The rocksalt and  $Cmcm$  structures. The atoms in the basis of  $Cmcm$  are labelled 1 to 4.

For  $Cmcm$  the lattice generators and basis vectors are the same as above but now both atomic species are allowed to have different internal parameters  $u_1$  and  $u_2$ . The resulting structure is the same as the one recently proposed for ZnTe-III [2] and for a high-pressure phase of CdTe [3], with space group  $Cmcm$ . A representation of the  $Cmcm$  structure is given in figure 1. The atoms in  $Cmcm$  are still contained in flat (010) rocksalt-like planes but the rows of atoms along the [100] direction within each plane are slightly puckered as a result of the different values of  $u_1$  and  $u_2$ . Both  $u_1$  and  $u_2$  may adopt values between 0 and 1 and, aside from a difference in orientation, an identical structure is obtained for  $u_{1/2} = \pm \delta u_{1/2}$ , as well as for  $u_{1/2} = 1 \pm \delta u_{1/2}$ . Note that for  $u_1 = u_2 = 0.5$  the arrangement of atoms is approximately hexagonal (with the  $c$  axis in the  $x$  direction) and that  $u_1 = u_2 = 0, b/a = c/a = 1$  corresponds to the rocksalt case. The distances and identity of close neighbours depend on the values of  $u_1$  and  $u_2$ , as well as on  $b/a$  and  $c/a$ . Note also that the structure resulting from interchanging the positions of the unlike atoms 3 and 4 of the basis in figure 1 corresponds to changing  $u_1$  and  $u_2$  to  $1 - u_1$  and  $1 - u_2$ , respectively. This observation is important because it allows us to investigate the effect of

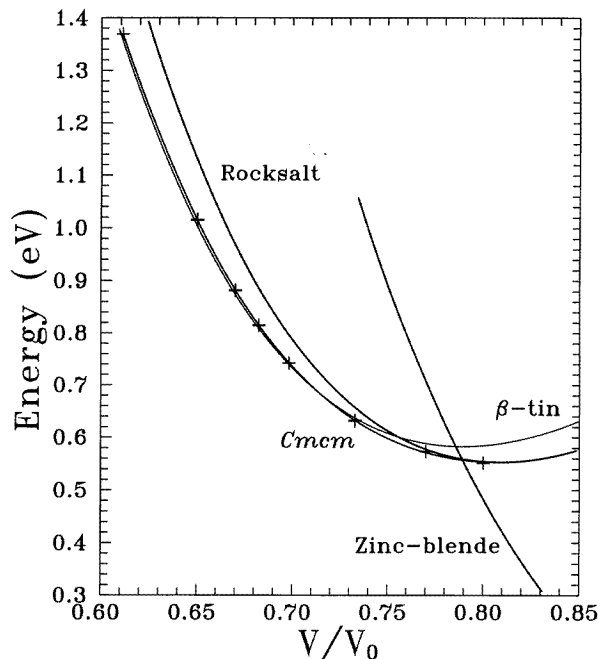
a different ordering of the atoms in the lattice of sites using the same set of lattice and basis vectors.

In order to investigate the phase stability we have performed calculations on the zinc-blende, rocksalt,  $\beta$ -tin and the  $Cmcm$  structures of GaAs. Other possible structures (NiAs, CsCl) reported as being those of various high-pressure phases in several III–V compounds have a much higher energy in the relevant pressure range and are not expected to be competing structures [9, 10].

We have performed local-density-approximation calculations using the plane-wave pseudopotential scheme. A review of this method and applications of it has been given by Pickett [11]. We used norm-conserving pseudopotentials for the  $\text{Ga}^{+3}$  and  $\text{As}^{+5}$  ions, and for Ga we included non-linear core-valence exchange-correlation corrections [13]. We used a basis set containing all plane-waves up to a cutoff energy of 24 Ry. For the Brillouin zone integrations, we used  $8 \times 8 \times 8$  k-point meshes for the semiconducting zinc-blende phase and  $16 \times 16 \times 16$ ,  $16 \times 16 \times 16$  and  $12 \times 12 \times 14$  meshes for the metallic rocksalt,  $\beta$ -tin and orthorhombic phases respectively. (All meshes are referred to the conventional choice of lattice vectors.) The uncertainties in the energy differences between phases are estimated to be less than 5 meV per formula unit. The values of the lattice constant and bulk modulus of the zinc-blende phase obtained using the above specifications ( $a_0^{the} = 5.610 \text{ \AA}$ ,  $B_0^{the} = 0.74 \text{ Mbar}$ ) are in excellent agreement with the experimental values ( $a_0^{exp} = 5.653 \text{ \AA}$ ,  $B_0^{exp} = 0.75 \text{ Mbar}$ ) [9]. The  $\beta$ -tin and  $Cmcm$  structures both have structural degrees of freedom and the energy was minimized with respect to all of them at each volume considered via the calculation of the stress tensor and the Hellmann–Feynman forces on the atoms. For the  $\beta$ -tin structure a value for the  $c/a$  ratio of about 0.55 was obtained, almost independent of pressure.

As a starting point for the relaxation of  $Cmcm$  we considered the structure proposed in [7] with the experimental parameters given in [5]. Analysis of the forces acting on each atomic species showed that this structure is unstable with respect to a distortion leading to the  $Cmcm$  structure, that is, to a structure for which the internal parameters of Ga and As are different. At the volume  $V = 31.538 \text{ \AA}^3$  per formula unit ( $V/V_0^{exp} = 0.698$ ), for which various structural information will be given below, we find  $b/a = 0.953$  and  $c/a = 1.049$ , which are in good agreement with the experimental values of  $b/a = 0.973$  and  $c/a = 1.055$  [5]. The calculated values of the internal parameters  $u_{As} = 0.317$  and  $u_{Ga} = 0.377$  bracket the experimental value of  $u_{As} = u_{Ga} = 0.35$  [5], which, however, assumed the  $Pmm2$  structure. At this volume, our relaxed  $Cmcm$  structure is about 52 meV per formula unit lower in energy than the rocksalt structure, and this difference increases as the volume is decreased.

In figure 2 we show the calculated energy–volume curve for the  $Cmcm$  structure along with those of the  $\beta$ -tin and rocksalt phases. Interestingly, we find the new structure to be very similar in energy to the  $\beta$ -tin structure in a large range of volumes investigated, with  $\beta$ -tin being marginally lower in energy at the lower volumes considered, and the  $Cmcm$  structure being lower at the largest ones. Similarly to previous theoretical calculations on GaAs [6], the bottom of the  $E$ – $V$  curve of the rocksalt structure lies below (30 meV per formula unit) the one for the  $\beta$ -tin structure, and as the volume is reduced the  $\beta$ -tin structure becomes energetically favoured over the rocksalt structure. However, we find that the crossing of both  $E$ – $V$  curves occurs at a somewhat higher volume than in earlier calculations. For example, at the volume  $V/V_0^{exp} = 0.733$  the energy of the  $\beta$ -tin structure is already about 16 meV per formula unit below the energy of the rocksalt structure. Consistent with this fact our calculations indicate that the zinc-blende structure becomes unstable to the  $Cmcm$

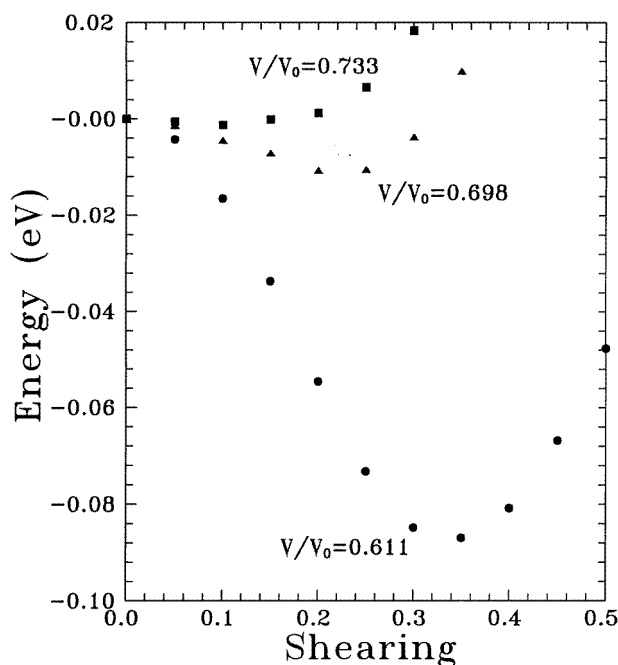


**Figure 2.** The energy,  $E$ , in eV per formula unit versus the volume,  $V$ , for the structures of GaAs studied. The volume is given in terms of the reduced volume  $V/V_0^{exp}$ , where  $V_0^{exp} = 45.168 \text{ \AA}^3$  per formula unit is the experimental zero-pressure volume of zinc-blende GaAs [9].

structure at a pressure of about 120 kbar and it becomes unstable to the rocksalt structure at the somewhat larger pressure of 130 kbar. At a pressure of about 120 kbar both the energy and enthalpy curves of  $\beta$ -tin and  $Cmcm$  are very close. Early experimental studies placed the I $\rightarrow$ II transition at about 170 kbar [5]. A more recent experimental study focused on the onsets of the forward and reverse transitions concluded that GaAs-I (zinc-blende) becomes unstable to GaAs-II at a lower pressure of  $120 \pm 15$  kbar [4], which coincides with our value. The calculated volume reduction at the transition,  $\delta V/V$ , is 0.176 which is also in good agreement with the reported experimental value of 0.172 [5].

The closeness in energy of the  $\beta$ -tin and  $Cmcm$  phases at the lowest volumes investigated is surprising because the structures are not closely related, differing even in the identity of the nearest neighbours. The binary  $\beta$ -tin (or A5) structure is roughly sixfold coordinated in the whole range of volumes investigated, with four unlike neighbours and two slightly farther like neighbours (for a volume  $V/V_0^{exp} = 0.698$ ,  $a = 4.8579 \text{ \AA}$ , the distances are  $0.5186a$  and  $0.5500a$  respectively). The degrees of freedom of the  $Cmcm$  structure allow different coordination numbers ranging from four to eight. Experimentally GaAs-II has been reported as a sixfold coordinated structure [5], and indeed we find the relaxed  $Cmcm$  structure to be roughly sixfold coordinated at the volume reported experimentally in [5], with all nearest neighbours being unlike atoms. The six nearest neighbours of either the Ga or As atoms (at the volume  $V/V_0^{exp} = 0.698$ ,  $a = 5.0158 \text{ \AA}$ ) comprise two atoms at a distance of  $0.5002a$ , one at a distance of  $0.5087a$ , two at a distance of  $0.5101a$ , and the farthest neighbour at  $0.5399a$  (which might be considered a second-nearest neighbour, leaving the close coordination as only fivefold). ‘Next-nearest’ neighbours are all like atoms: there are

two for each As atom at a distance of  $0.5960a$  and two for each Ga atom at a distance of  $0.5778a$ . Thus each atom has eight neighbours in the range between  $0.5a$  and  $0.6a$  arranged in a distorted simple hexagonal manner. The next eight close neighbours, which are like atoms, are at distances  $\sim 0.71a$ – $0.72a$ . At this volume the internal parameters are  $u_{As} = 0.317$  and  $u_{Ga} = 0.377$ . The internal parameters of *Cmcm* tend to increase as the volume is reduced, which reflects a tendency to increase the coordination with increasing pressure. (Note that coordination number increases towards eight which is the coordination number of the higher-pressure phases.)



**Figure 3.** Difference in energy with respect to the rocksalt structure at four different volumes, as a function of the shearing of the (010) planes. The shape of the rocksalt cell has been held fixed and no puckering of the atomic chains (along the [100] direction) has been allowed.

We have also investigated the driving forces for the distortion from rocksalt to *Cmcm*. This distortion has three separate components; the orthorhombic distortion of the cell shape, the shearing of the (010) planes and the puckering of the atomic chains. We have performed calculations imposing each one of the three components separately on the rocksalt structure. We find that rocksalt GaAs is unstable to the shearing of the (010) planes, whereas it is stable to the cell distortion and the puckering. However, when a shear is imposed anisotropic components of the stress and forces on the atoms appear which result in the cell distortion and puckering. We therefore view the shearing as the primary driving force favouring *Cmcm* over rocksalt and the cell distortion and the puckering are consequences of the shearing instability. In figure 3 we plot the difference in energy with respect to the rocksalt structure considering *only* shearing of the (010) planes within the rocksalt cell. The Ewald term in the total energy strongly favours the structures with shearing,  $u$ , close to 0.5. (The destabilizing effect of the Ewald term in the rocksalt structure is common to all the binary compounds.) The kinetic and Hartree terms further favour the distortion but a

delicate cancellation with the remaining terms in the total energy occurs which results in the actual minimum energy structure. The instability of the rocksalt structure increases as the volume decreases. However the gain in energy in figure 3 is small in comparison to the fully relaxed *Cmcm* structures because the relaxation of the shape of the rocksalt cell and the puckering of the atomic rows have not been taken into account. At the volume  $V/V_0^{exp} = 0.698$  the relaxed *Cmcm* structure is 52 meV per formula unit lower in energy than the rocksalt structure, and the majority of this energy reduction (38 meV) is achieved by shearing plus cell distortion. Also note that the minima in figure 3 are at values of  $u$  somewhat smaller than the values of  $u_1$  and  $u_2$  for the fully relaxed structures.

A further interesting question is whether the ordering of As and Ga atoms on the lattice is precisely as shown in figure 1. In ZnTe-III, for example, almost the same quality of fit to the experimental diffraction pattern was obtained assuming the reordered structure with atoms 3 and 4 on figure 1 interchanged [2]. As noted above, this reordering preserves the symmetry, and is the only other possible ordering with the four atoms per unit cell indicated by experiment. However, our calculations indicate that this structure is unstable and upon relaxation it gradually returned to the original *Cmcm* structure. (This is expected since contrary to the normal case the atoms in the reordered structure have like nearest neighbours.)

In conclusion, we have performed a first-principles pseudopotential study of the *Cmcm* phase of GaAs which is an orthorhombic distortion of the rocksalt structure. We propose that this *Cmcm* structure corresponds to the experimentally observed GaAs-II phase. Our calculations show that this phase becomes thermodynamically stable at a pressure of 120 kbar, in agreement with the experimental data for GaAs-II. Furthermore the volume decrease at the transition and the structural parameters ( $b/a$ ,  $c/a$  and internal parameters) also agree with the available experimental data. The *Cmcm* structure can be related to the rocksalt structure by a shearing of alternate (010) planes and a puckering of [100] rows, accompanied by an orthorhombic cell shape distortion. Rocksalt GaAs is unstable to such shearing of (010) planes, which is the driving force leading to a *Cmcm* structure, while the puckering and cell shape distortions are consequences of the shearing. For such binary compounds the structure suggested in [7] is always unstable to puckering, which leads to a *Cmcm* structure, with the degree of distortion depending on the particular compound. We note that this *Cmcm* structure has recently been identified as that of ZnTe-III [2] and a high-pressure phase of CdTe [3]. This structure corresponds to the simplest possible case of such a distortion and more complicated versions can exist, such as the orthorhombic InSb-IV structure which involves a more complicated pattern of shearing six (010) planes rather than shearing only alternate planes [1], although the space group is still *Cmcm*. We expect stabilization of *Cmcm*-type structures by such a shearing mechanism (with puckering and cell distortion) to be common among III-V and II-VI compounds. Preliminary studies by us on InP and InAs show the same instability of the rocksalt phase (towards shearing of (010) planes), leading to the *Cmcm* structure as in GaAs. For these compounds the rocksalt phase had the lowest enthalpy at high pressure among all the phases considered in previous studies and thus their true high-pressure structure should also be *Cmcm* [14].

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- [14] After the completion of this work we became aware of preliminary experimental work (Nelmes R J *et al* 1995 *J. Phys. Chem. Solids* **56** 539) that lends support to the existence of a stable *Cmcm* phase in these compounds. We thank Professor Nelmes for bringing his work to our attention.