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LETTER TO THE EDITOR

Structural and electronic properties of molten GaAs

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Abstract. We present the first microscopic investigation of the atomic and electronic structure of a molten-compound semiconductor. Our approach is based on pseudopotential-derived interatomic forces, a molecular-dynamic simulation of the atomic structure, and a supercell linearised-muffin-tin-orbital calculation of the electronic density of states. Our results for the atomic structure of molten GaAs are in good agreement with recent neutron-diffraction data. We find that the complex structure of the metallic melt arises from the modulation of the random packing of the atoms by the Friedel modulations in the effective interatomic interactions. The arrangement of the atoms is chemically random and shows only weak angular correlations. This has important consequences for the electronic structure. The loss of bond-orientational order on melting leads to the disappearance of the optical (covalent) gap and to the semiconductor–metal transition. The large number of like-atom ('wrong') bonds causes the filling of the ionic gap characteristic of the compound semiconductors. The s bands of both As and Ga are broadened so that the As s band is no longer separated from the rest of the valence band.

In the crystalline state the light group-IV elements Si and Ge and the iso-electronic III–V and II–VI compounds are semiconducting and fourfold coordinated at low temperatures and pressures. Their structure and electronic properties are usually explained in terms of the formation of sp^3 hybrids pointing into the direction of the tetrahedral bond angles. The application of pressure induces a semiconductor–metal transition, associated with an increase of the coordination number from four to six [1, 2]. The liquid phase of both Si and Ge is also metallic, with coordination numbers of $N_c = 6.5 \mp 0.5$ [3]. On the other hand, the II–VI compounds, such as CdTe, remain semiconducting after melting, the coordination number being $N_c = 3-4$ in the liquid phase [4]. The III–V compounds show an intermediate behaviour: liquid GaAs, for example, is metallic, but shows only a small increase of the coordination number to $N_c = 5.5 \mp 0.5$ [5]. This raises the question whether the structural and electronic properties of the molten III–V compounds are different from those of the liquid group-IV elements. Indeed, a comparative study of the structure of amorphous Ge and amorphous GaAs has revealed significant differences in the medium-range order [6]: the structure of the amorphous compound is better described by a model containing only even-membered rings (as anticipated from the partially heteropolar character of the bonds), while the structure of amorphous Ge is better accounted for by a model allowing at least for a certain proportion of odd-membered rings.

The correct description of the complex structures of the liquid polyvalent elements and their alloys is a subject of ongoing debate [7–10]. Although recent photoemission

experiments [11] have shown that the electronic density of states (DOS) of a liquid element such as Ge are different from that of any of its crystalline phases, crystalline concepts for the short- and medium-range order are still under consideration [5, 7, 8]. On the other hand, we have been able to demonstrate in a series of molecular dynamics studies of liquid Ga [12], Si [12], Ge [10], and As [9] that the complex, open structures of the liquid polyvalent elements are more convincingly interpreted as arising from the modulation of the random packing of the atoms by the Friedel oscillations in the effective interatomic interactions. The important point is that the same concept was used some years ago by Hafner and Heine [13] to explain the trends in the crystal structures of the s, p-bonded elements.

In this Letter we present detailed theoretical investigations of the structural and electronic properties of molten GaAs. The approach is based on the same simple form of the effective interatomic interactions as used by Hafner and Heine [13] in their study of the crystal structures, and in our recent investigations of the liquid structures of the elements [9, 10, 12]. The atomic structure is calculated via molecular dynamics. The electronic DOS is calculated using a supercell linearised-muffin-tin-orbital (LMTO) technique [10, 12, 14]. Our results for the atomic structure are in good agreement with the available neutron-diffraction data [5]: the predicted bond length ($d_1 = 2.57 \text{ \AA}$) and coordination number ($N_c = 5.54 \mp 0.5$) agree well with those derived from the diffraction experiments ($d_1 = 2.56 \text{ \AA}$, $N_c = 5.5 \mp 0.5$). The coordination number is lower than that calculated for liquid Si and Ge ($N_c = 6.5 \mp 0.5$). In this Letter coordination numbers are calculated by integrating over the symmetric part of the first peak in the radial distribution function. This yields somewhat lower numbers than the integration up to the first minimum of the full radial distribution function used in our work on liquid Ge [10]. Distinct differences are also found in the electronic structures of liquid Ge and GaAs. In the liquid element the breaking of the bond-orientational order leads not only to the disappearance of the covalent gap (which arises from the bonding–antibonding splitting of the sp^3 hybrids), but also to a nearly complete suppression of s–p hybridisation in the valence band. The s and p bands are separated by a deep minimum in the DOS [10], in full agreement with photoelectron spectroscopy [11]. In crystalline GaAs the polarity of the bonds leads to a first valence band which is strongly As s-like and separated from the rest of the valence band by an ‘ionic’ gap. Ga s and As p states interact in the second valence-band region, while Ga p and As p states dominate in the upper valence band [15]. In liquid GaAs we find the overall structure of the DOS to be similar, albeit with two important modifications: (i) the breaking of the directed bonds by thermal disorder leads to a disappearance of the covalent gap, in complete analogy to liquid Ge; (ii) the ‘ionic’ gap is also filled. This is in direct contrast to liquid Ge, where a pseudo-gap separating the s and p states is *created* at the semiconducting crystal–liquid metal transition. We discuss these differences in the electronic structure in relation to the atomic structure of the melt and we argue that the filling of the ionic gap in liquid GaAs is due to the existence of a large number of ‘wrong’ bonds between like atoms.

The interatomic potentials $\Phi_{ij}(R)$ and the volume energy $E_0(V)$ have been calculated using standard second-order perturbation theory, based on the simple empty-core model potential [16] and the Ichimaru–Utsumi form of the dielectric screening [17]. The core radii follow systematic trends across the periodic table; their choice has been discussed in connection with the elemental crystalline [13] and liquid [9, 12] structures. The same values ($R_c(\text{As}) = 0.53 \text{ \AA}$, $R_c(\text{Ga}) = 0.45 \text{ \AA}$) are used in the present work. The pair potentials calculated for the liquid compound ($T = 1523 \text{ K}$, number density $n = 0.0447 \text{ \AA}^{-3}$) are quite similar to their form in the pure elements (figure 1). The nearest-

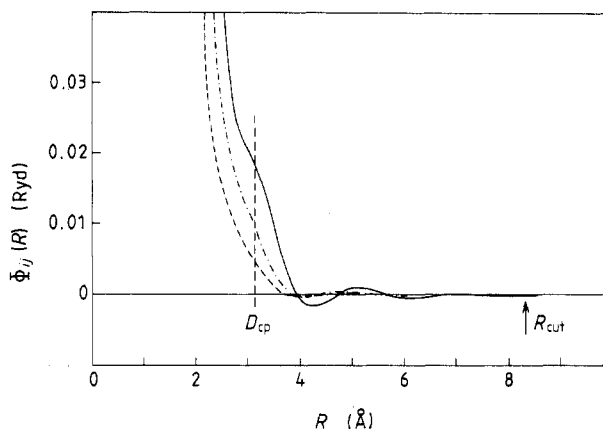


Figure 1. Interatomic interactions in liquid GaAs. The broken curve indicates Ga-Ga interactions; the chained curve, Ga-As; the full curve As-As. The vertical line marked D_{cp} represents the nearest-neighbour distance in a 12-coordinated close-packed structure. R_{cut} the cut-off of the potential used in the molecular-dynamics calculations.

neighbour distance D_{cp} in a close-packed structure with coordination number $N_c = 12$ falls on a repulsive hump of the As-As interaction, and into a region where the curvature of the As-Ga and Ga-Ga potentials is very small. Hence as in pure Ga, Ge and As we find that it is energetically favourable to move the atoms from D_{cp} into the neighbouring potential-energy minima (or into the inflections of the potentials). This leads to a splitting of the first coordination shell into two sub-shells centred roughly at $R_1 = D_{cp} - \lambda_F/2$ and $R_2 = D_{cp} + \lambda_F/2$ where $\lambda_F = 2\pi/2k_F$ is the Friedel wavelength (k_F is the Fermi momentum). For the given density of GaAs we calculate $D_{cp} = 3.18 \text{ \AA}$ and $\lambda_F = 1.81 \text{ \AA}$, thus $R_1 = 2.28 \text{ \AA}$ and $R_2 = 4.09 \text{ \AA}$. Even allowing for the density change on melting, this is in reasonable agreement with the interatomic distances in crystalline GaAs with the zincblende structure ($d_1 = 2.448 \text{ \AA}$ and $d_2 = 3.997 \text{ \AA}$). A lower bound to the coordination number may be estimated from the relation $(N_c + \frac{1}{3})^{1/3} = (R_1/D_{cp})$ [13, 16]. In our case this yields $N_c = 3.8$. Thus we find that this simple set of potentials is sufficient to explain the stability of the zincblende structure of crystalline GaAs relative to the close-packed metallic structure. Needless to say this argument explains only the static stability. As for diamond-structure Si and Ge, some transverse acoustic phonon branches are unstable in GaAs if only volume and pair forces are considered. However, this is irrelevant to the following investigations, since shear waves are overdamped in the melt anyway (for a more detailed discussion of this point, see [10]).

The structure of molten GaAs has been calculated using classical constant-energy molecular dynamics (MD) for different ensembles containing between 64 and 1024 atoms in a periodically repeated cubic box (for a detailed description of the MD routine see [10]). The simulation started with the atoms arranged on the sites of a simple cubic lattice; the system was first molten at $T = 2000 \text{ K}$ and then slowly cooled to $T = 1523 \text{ K}$. The pair potentials were truncated at $R_{cut} = 8.3 \text{ \AA}$ for the largest and at $R_{cut} = 5.8 \text{ \AA}$ for the smallest ensemble.

The partial pair correlation functions $g_{ij}(R)$ and static structure factors $S_{ij}(q)$ are again rather similar to the pure elements (figure 2). The distribution of the two atomic species is essentially random, the partial coordination numbers being $N_c(\text{Ga-Ga}) =$

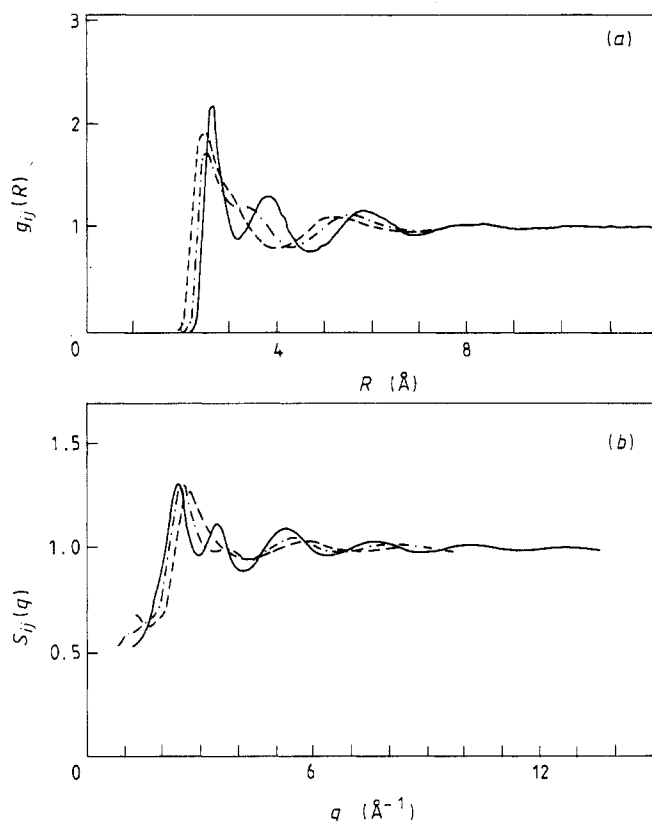


Figure 2. (a) Partial pair correlation functions $g_{ij}(R)$ and (b) static structure factors $S_{ij}(q)$ for liquid GaAs at $T = 1511$ K. The broken curve indicates Ga-Ga interactions; the chained curve, Ga-As; the full curve As-As.

3.29, $N_c(\text{Ga-As}) = 2.61$, $N_c(\text{As-As}) = 2.56$, $N_c(\text{As-Ga}) = 2.62$. The average total coordination number $N_c = 5.54 \pm 0.5$ agrees well with the value derived from the neutron diffraction data ($N_c = 5.5 \pm 0.5$) [5]. The first two peaks in the As-As correlation function correspond very well to the inflection and to the first minimum in the As-As pair potential. The small curvature of the Ga-Ga potential leads to an asymmetric first peak in $g_{\text{Ga-Ga}}(R)$ with a shoulder on its right-hand side. In the $S_{ij}(q)$ the second peaks of the As-As and Ga-As structure factors fall very close to $q_2 \approx 2k_F = 3.47 \text{ \AA}^{-1}$, the first peaks near $q_1 \approx 2\pi/R_1 = 2.7 \text{ \AA}^{-1}$ (slightly shifted because of the steeply repulsive short-range potentials and of atomic-size differences). This shows that like the structures of liquid Ga, Si, Ge, and As, the structure of the liquid compound may be considered as arising from the modulation of the random packing of atoms by the Friedel oscillations in the effective interatomic potentials. In a binary liquid the strength of this modulation is set by the on-Fermi-sphere matrix elements of the pseudopotentials, which determine the amplitudes of the Friedel oscillations.

The neutron-weighted reduced pair distribution function $G(R) = 4\pi nR(g(R) - 1)$ and static structure factor $S(q)$ are shown in figure 3, together with the neutron-diffraction data of Bergman and co-workers [5]. We find a good agreement between theory and experiment, with a slight tendency to overestimate the medium-range correlations

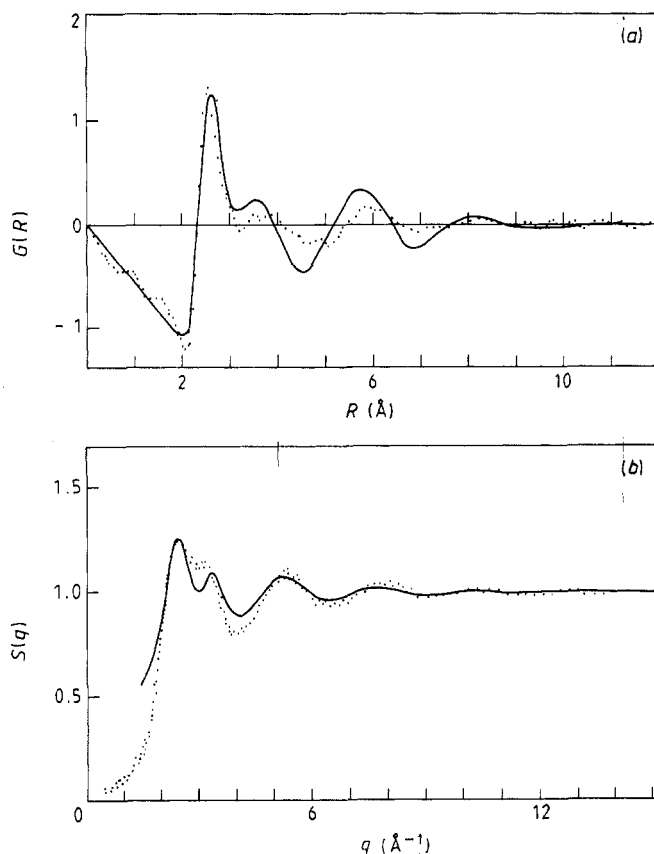


Figure 3. (a) Neutron-weighted reduced radial distribution function $G(R) = 4\pi nR(g(R) - 1)$ and (b) static structure factor $S(q)$, for liquid GaAs at $T = 1511$ K, full curves, compared with the neutron-scattering data at $T = 1523$ K taken from Bergman and co-workers [5], dotted curves.

that was also observed in liquid Ge. This could be related to the fact that we have ignored all effects associated with a finite mean free path of the electrons, which would lead to a slight damping of the Friedel oscillations [18]. It is interesting to compare liquid GaAs and liquid Ge. In normal hard-sphere-like liquids the ratio of the positions of the first and second peaks in $S(q)$ is $q_2/q_1 = 1.8$, but is substantially larger in low-coordinated liquids such as Si and Ge ($q_2/q_1 = 2.05$) and As ($q_2/q_1 = 2.3$). The value for GaAs is $q_2/q_1 = 2.16$. According to Georghiu and co-workers [6] this ratio is sensitive to the medium-range order, in particular to the fraction of odd-membered rings and hence to the number of 'wrong' bonds. An even more pronounced difference is found in the height of the diffraction peaks. In a normal liquid close to freezing one has $S(q_1) = 2.8$, but we find only $S(q_1) = 1.5$ in Si, Ge, and As, and even $S(q_1) = 1.25$ in GaAs. The low amplitude of the structure factor reflects the fact that, due to the interference between the two characteristic length scales (the distance R_1 of closest approach and the Friedel wavelength λ_F), all structural correlations beyond a range of 8–10 Å are destroyed. This destructive interference is even more effective in a binary liquid, because of the differences in atomic size and in the amplitudes of the oscillations in the set of pair interactions.

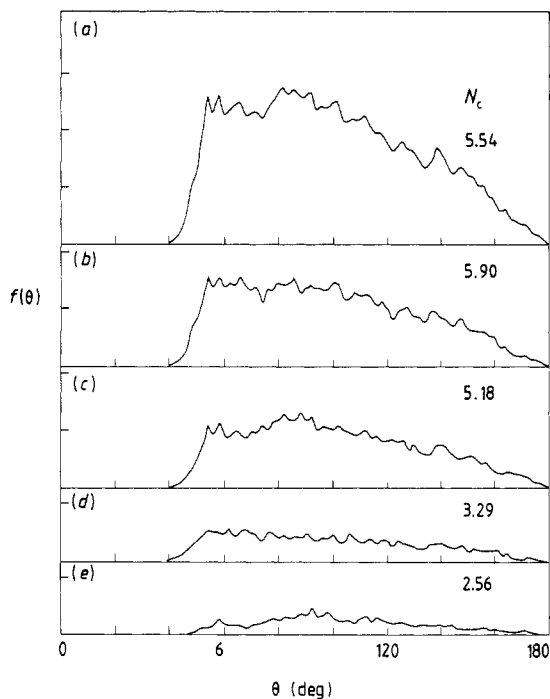


Figure 4. (a) The total and (b)–(e) the partial bond-angle distribution functions $f(\theta)$ in liquid GaAs at 1511 K. (b), XGaX; (c) XAsX; (d), GaGaGa; (e), AsAsAs.

The higher degree of disorder in liquid GaAs compared to liquid Ge is also evident from the bond-angle distributions (figure 4). The total $f(\theta)$ points to very weak angular correlations, beyond those imposed by steric reasons (the $f(\theta)$ s are normalised such that in the chaotic limit $f(\theta) \propto \sin\theta$). Only in the distributions of the angles formed by like-atom bonds are small differences found: Ga–Ga bonds tend to form 60° angles, indicating the existence of a certain number of isosceles-triplets of Ga atoms. Only a few such small bond angles are found for As–As bonds, and the maximum of the partial bond-angle distribution is shifted to larger angles, i.e. close to the bond angle in crystalline and liquid As [9].

Our finding that liquid GaAs is more disordered than liquid Ge is in agreement with the known entropies of fusion: one has $S_f = 7.2 \text{ cal mol}^{-1} \text{ K}^{-1}$ for Si and Ge, but $S_f = 8.6 \text{ cal mol}^{-1} \text{ K}^{-1}$ for GaAs. In any case, the largest part of this abnormally large heat of fusion comes from the delocalisation of the electrons in the solid semiconductor–liquid metal transition, but the further increase from Ge to GaAs is probably due to the chemical disorder.

The electronic DOS for crystalline and liquid GaAs calculated using the scalar-relativistic LMTO in the atomic-sphere-approximation (ASA) [14] are shown in figure 5. The calculation for crystalline GaAs was performed with empty muffin-tin spheres placed into the octahedral and tetrahedral holes of the zincblende lattice, using the ‘combined correction term’ [14] and the ‘artificial Darwin shift’ introduced by Bachelet and Christensen to account for the width of the covalent energy gap [15]. The calculation for liquid GaAs has been performed for a periodically repeated supercell containing 64 atoms, the atomic positions in the cell being generated in an MD simulation. The crystalline DOS was calculated using the tetrahedron method, based on 89 k -points in the irreducible part of the Brillouin zone. The liquid DOS was calculated from 4 k -points

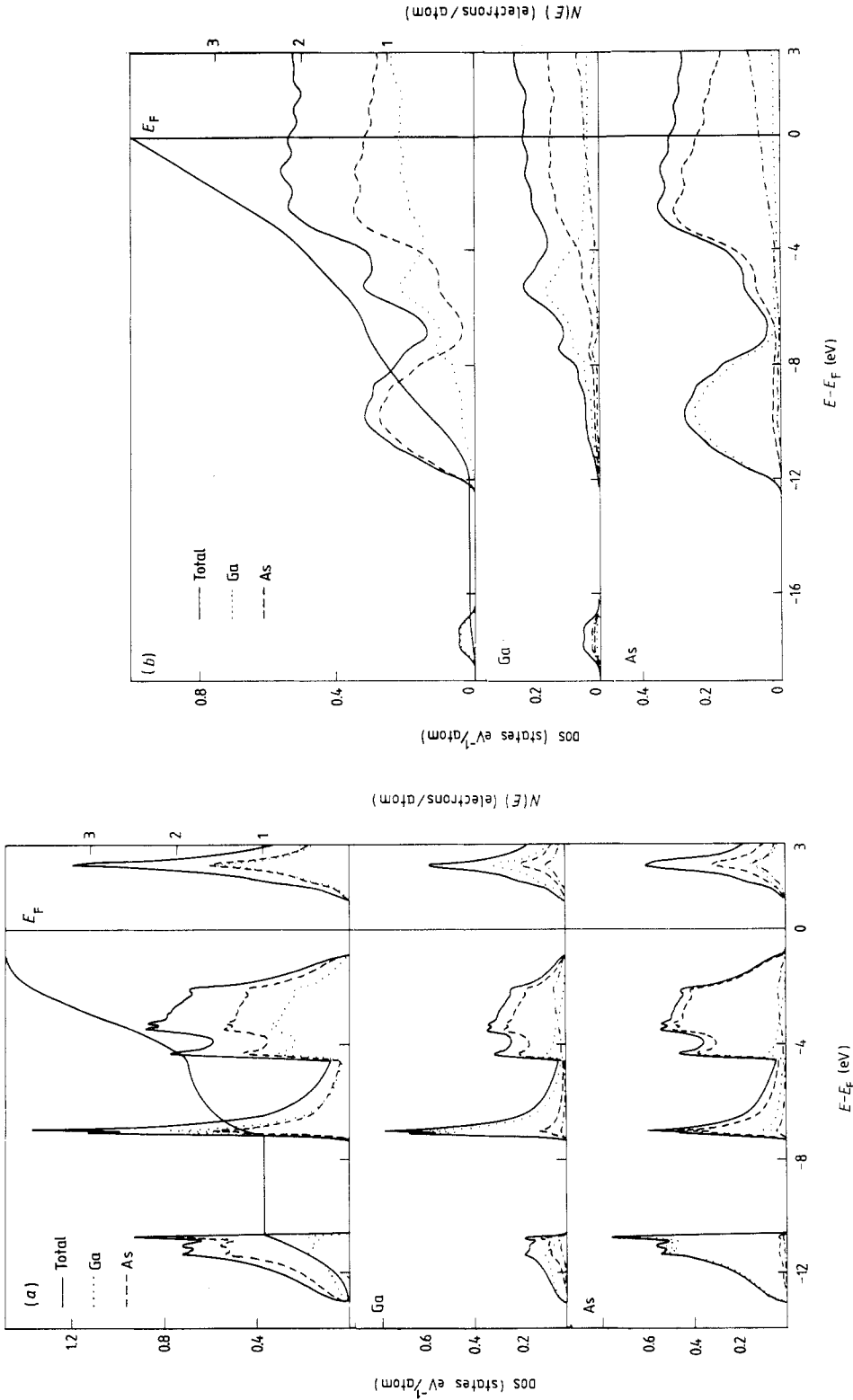


Figure 5. Total, site- and angular-momentum decomposed electronic density of states in (a) crystalline and (b) liquid GaAs at 1523 K. For the site-decomposed DOS the full curve shows the partial DOS, and the dotted, broken and chain curves the s, p and d contributions. The right-hand-scale shows the integrated DOS.

(the corners of the irreducible wedge of the Brillouin zone belonging to the 64-atom supercell), a Gaussian broadening with $\sigma = 0.2$ eV being used to smooth the discrete eigenvalue spectrum. For further details, see our work on liquid Ge [10].

The DOS of crystalline GaAs shows the characteristic features discussed above. In the DOS of liquid GaAs we find some low-lying states close to -17 eV (relative to the Fermi energy). These are resonant bound states localised in the shortest bonds. They are a consequence of the large scatter of the nearest-neighbour distances in the melt. If an extended configuration average were taken, these resonant states would form a smooth tail to the lower edge of the valence band. Here we calculated the DOS only for two different atomic configurations. Except for these resonant bound states, no significant differences in the DOS derived from different 64-atom models have been found, in agreement with previous experience on other liquid [10, 12] and amorphous [19] metals. The changes in the valence band on melting are rather interesting. The width of the band is the same in the crystal and in the liquid, $W = 12.1$ eV, this being only slightly larger than the free-electron band width $W_{FE} = 11.6$ eV. Both the covalent and the ionic gap disappear on melting, but the characteristic three-peaked structure of the DOS is preserved. However, this apparent similarity of the electronic DOS in crystalline and liquid GaAs should not be taken as an indication that the atomic structure is similar as well. At this level, the structure of the DOS is determined mainly by the polarity of the bond. More significant for the local order is the filling of the ionic gap.

In liquid Ge and in liquid GaAs the directed bonds via overlapping sp^3 -hybrids are broken by thermal disorder. At the given density and coordination of liquid Ge the overlap of the atomic s and p states is not large enough to broaden the atomic energy levels into a free-electron-like band, and hence s and p states are separated by a pseudo-gap [10, 11]. At a coordination number of six a free-electron-like hybridisation is only achieved at the much higher density of the simple-hexagonal high-pressure polymorph. In liquid GaAs thermal disorder destroys not only the bond-orientational order, it also relaxes the constraint of forming unlike-atom bonds only. The width and shape of the As s and Ga s bands, which is determined in the zincblende lattice by second-neighbour interactions, is greatly affected by the introduction of 'wrong' bonds. The nearest-neighbour As-As and Ga-Ga interactions induce a strong broadening of both s bands that leads to the filling of the ionic gap. The partial DOS on the As-sites is now quite similar to that in liquid As [12], as expected from the similarity in the local environment. The partial Ga DOS, however, is different from that in liquid or crystalline Ga: the low-energy tail arises from the Ga-As interactions, the minimum in the DOS at about -4 eV separating the s- and p-dominated sub-bands indicates that at a Ga-Ga coordination number of $N_c = 3.29$ the interaction is not yet strong enough to achieve the nearly-free-electron hybridisation characteristic of liquid Ga [12, 20] or of the crystalline high-pressure phases ($N_c = 8$ liquid Ga).

Our results are in good agreement with recent investigations of the electronic structure at defects in amorphous GaAs [21, 22]. It has been shown that the main effect of 'wrong' bonds is to introduce a broadening and a bonding-antibonding splitting of the bands that tends to narrow the ionic gap.

To our knowledge this is the first theoretical investigation of the structural and electronic properties of a molten semiconductor compound. We find that in GaAs melting destroys not only the bond-orientational order characteristic of the tetrahedral semiconducting crystal, but in addition induces a strong chemical disorder and the formation of a many like-atom ('wrong') bonds. However, the liquid alloy should not be termed substitutional because the partial correlation functions and bond-angle

distributions show the local environments of the As and Ga atoms are distinctly different. In the electronic structure the loss of orientational ordering causes the disappearance of the covalent gap, the large number of 'wrong' bonds leads to the filling of the ionic gap. Our results for the atomic structure are well confirmed by neutron diffraction data. We hope that this work will stimulate experimental investigations of the electronic structure of molten GaAs.

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