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α-gallium: A metallic molecular crystal

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We present a first-principles theoretical study of the atomic and electronic structures, and of the zero-temperature phases of gallium. The picture of α-Ga that emerges is of a metallic molecular crystal with a strong Ga_2 covalent bond and weaker intermolecular forces. This picture is supported in detail by the charge density, the electronic structure, and differential bond stretching under pressure. Anomalous features of α-Ga, such as the Knight shift, anisotropic Fermi-surface effects, and optical absorption find a consistent explanation. Accurate x-ray measurements should reveal the Ga_2 covalent bonds.

Elemental molecular solids are expected to turn metallic upon application of a sufficiently large external pressure. It is generally assumed that during this process the molecular bond and the associated band gap disappear at the same time as the metal-insulator transition occurs. Very recently, however, it has been found that in the case of crystalline I_2 the metal-nonmetal transition occurs at a lower pressure than that necessary to induce molecular dissociation.[1] This provides an intriguing example of a crystal that at the same time is molecular and metallic.

Based on an *ab initio* study of lattice and electronic properties, we propose in this paper that the α phase of Ga is in fact another realization of a phase in which a molecular character and metallic conduction coexist. The α-Ga lattice, stable at ambient pressure, is base-centered orthorhombic with eight atoms in the cubic unit cell. A peculiar feature of this structure is that each atom has only one neighbor in the first coordination shell centered at 2.44 Å. The second, third, and fourth shells each contain two atoms, and are 0.27, 0.30, and 0.39 Å further apart, respectively. These six atoms all lie on a strongly buckled plane that is about 1.49 Å thick. From this point of view, the α-Ga structure could be regarded as consisting of strongly buckled parallel planes connected by short bonds between the first neighbor atoms which lie in different planes. Other important crystal structures that will be considered here are Ga II, its fcc parent structure, and finally β-Ga. Ga II can be obtained from α-Ga upon application of an external pressure [of about 35 kbar at $T=0$ K (Ref. 2)], and is a tetragonally distorted fcc structure.[3] β-Ga on the other hand is monoclinic and can be obtained as a metastable state by supercooling liquid Ga.[4] All the relevant phases are metallic in the range explored and there are no signs of density-induced metal-nonmetal transitions. The relative stability of these structures was studied by means of total-energy calculations within the local-density-approximation (LDA) scheme.[5] We have used a first-principles nonlocal norm-conserving pseudopotential of the Kleinman-Bylander form,[6] constructed from the tables of Stumpf, Gonze, and Scheffler.[7] We retained both s and p nonlocality, and expanded the Kohn-Sham electronic wave functions in plane waves up to an energy cutoff of 14 Ry. Very fine differences between total energies of different structures are difficult to obtain with the usual **k**-summation scheme, at least with a manageable number of **k** points. In order to maximize error cancellation by taking energy differences, we have decided instead to use only the $\mathbf{k}=0$ point of rather large supercells containing roughly the same number of atoms, namely 72 for α-Ga, Ga II, and fcc Ga, and 64 for the β-Ga structure. An additional advantage of this choice is that in a large supercell the ions can be allowed to relax from their ideal positions, which greatly enhances the variational flexibility of our search. Finally, our calculation provides a useful start for future studies of the disordered and liquid phases of Ga, where it will be mandatory to consider large supercells. The results presented here are a small fraction of a much larger set for which convergence relative to cell size, number of **k** points, and energy cutoffs have been checked.[8]

First of all, we establish that for small pressures α-Ga dominates the $T=0$ K phase diagram. Our subsequent analysis of α-Ga shows: (i) a covalent bond between each Ga pair, (ii) a pseudogap in the electronic density of states at the Fermi level, (iii) very good agreement between theoretical predictions and experimental data on optical conductivity, and (iv) a measurable effect on the x-ray-related electronic-structure factor $S(\mathbf{k})$ induced by the covalent (molecular) bond.

a. Lattice stability. In Fig. 1, we report the energy per atom of various structures versus volume. The points have been obtained by allowing a full relaxation of the atomic positions and are interpolated with a Murnaghan-type equation. The α-Ga structure has the lowest energy, with $a=4.38$ Å, $b=4.39$ Å, and $c=7.43$ Å (to be compared with the experimental values $a_{\mathrm{exp}}=4.51$ Å, $b_{\mathrm{exp}}=4.52$ Å, and $c_{\mathrm{exp}}=7.64$ Å). This is the less-dense phase, corresponding to the formation of $\mathrm{Ga_2}$ molecular bonds (see below). In the lower panel of Fig. 1, we show how the shortest Ga-Ga distance, obtained by allowing relaxation of the atomic positions, varies with volume. The presence of a stiff $\mathrm{Ga_2}$ covalent bond is suggested by a slope that is $\sim 20\%$ lower than the overall averaged value, implying in turn that the $\mathrm{Ga_2}$ force constant is about twice as large as the average. The Ga II structure lies immediately above α-Ga in energy, with a pressure-induced transition α Ga→Ga II at ~ 60 kbar, in reasonable agreement with the experimental value. The fcc and β structures are found to lie higher in energy, quite close together and, at least for the values of density considered in the present calculations, are not reachable at $T=0$ K by applying pressure.

b. Electron density. In Fig. 2, we report the electronic density of states $D(\varepsilon)$ for α-Ga, β-Ga, and Ga II, as well as the charge density $\rho(r)$ for α-Ga and Ga II. All $D(\varepsilon)$ have been computed at the theoretical equilibrium zero-temperature density, using the self-consistent potential for each structure and a conventional diagonalization in the primitive cell for a large set of uniformly spaced $\mathbf{k}$ points. The $D(\varepsilon)$ of α-Ga clearly shows a psuedogap at the Fermi energy E_F. The connection between the pseudogap and covalency in α-Ga was discussed long ago by Heine.[9] The molecular $\mathrm{Ga_2}$ bonding is visible as a pileup of charge (see inset of Fig. 2). The residual states in the pseudogap are related to the overlap of the electronic wave functions along the buckled planes perpendicular to the molecular bond. These states lead to metallic behavior, which thus coexists with the molecular state. The flexibility of simultaneously forming two kinds of chemical bonds greatly contributes to the stability of this structure. Purely insulating molecular structures based on $\mathrm{Ga_2}$ are not favored, given the low-energy gain associated with a fully molecular bond. That the states in the gap are related to the in-plane electron motion is also suggested by the band structure of Fig. 3, as discussed below. Once the crystal reaches the Ga II structure, the covalent bonds disappear (inset of Fig. 2) as does the pseudogap at E_F. Both Ga II and β-Ga in fact show a nearly-free-electron behavior. The difference between the $D(E_F)$ of α-Ga and β-Ga is experimentally reflected in the Knight shift, which in β-Ga is about three times larger than in α-Ga.[10] We obtained a ratio of about 7 between the calculated values of $D(E_F)$. Although we have not attempted to estimate the

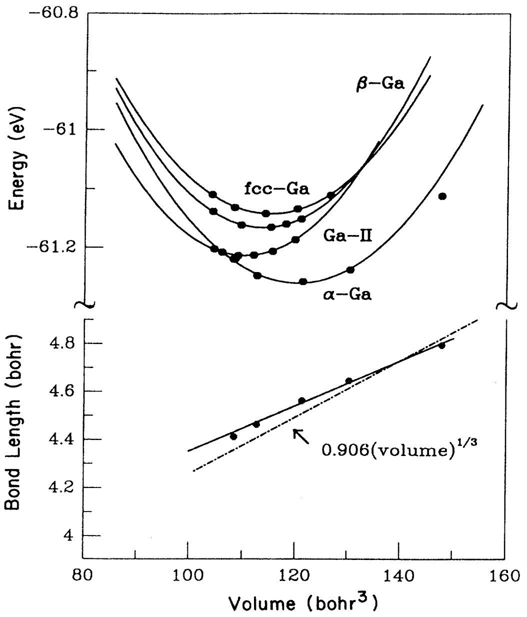

FIG. 1. Upper panel: α-Ga, Ga II, β-Ga, and fcc-Ga total energy as a function of volume. Lower panel: the α-phase Ga-Ga shortest distance as a function of volume (circles). The solid line is a guide to the eye. The dash-dotted line is the average atomic diameter.

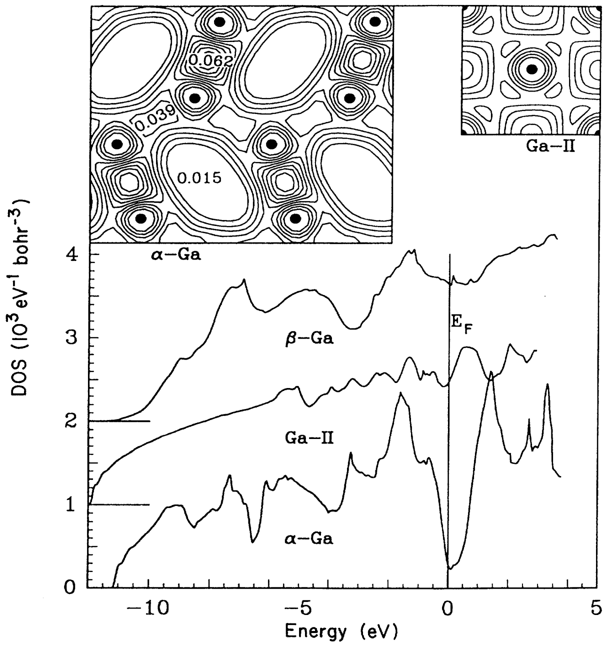

FIG. 2. Electron density of states for α-Ga, β-Ga, and Ga II. Note the deep pseudogap of α-Ga. The insets are the charge-density maps for α-Ga in the (100) plane and Ga II in the (001) plane (unit of electrons/bohr^3). Note the strong covalent $\mathrm{Ga_2}$ bond.

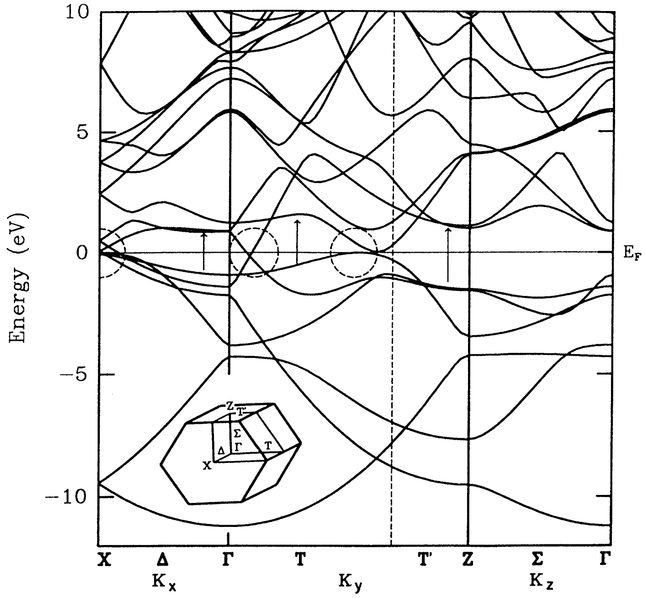

FIG. 3. The band structure of α-Ga along some high-symmetry lines. Circles indicate portions of the Fermi surface. Arrows denote important molecular bonding-antibonding optical transitions.

relative values of $|\Psi(0)|^2$ between α-Ga and β-Ga, the pseudocharge densities near the s core radius ($r_s = 1.27$ a.u.) are not unlike, which suggests that the difference in $D(E_F)$ is indeed the main factor.

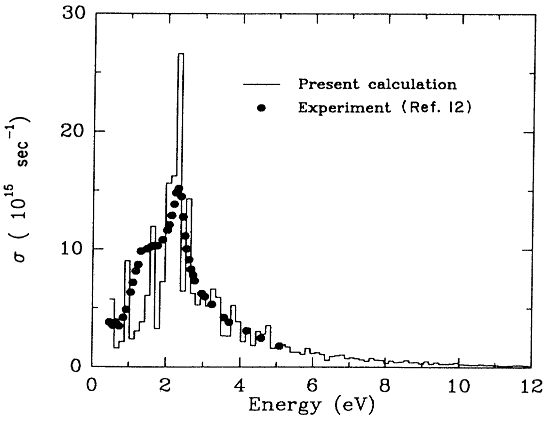

FIG. 4. Calculate (solid line), experimental (circles), and optical conductivity of α-Ga.

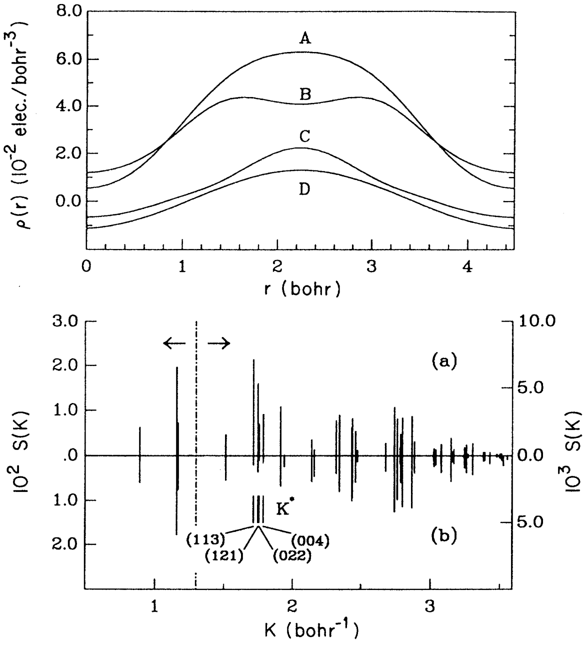

FIG. 5. Upper panel: The electron density along the Ga−Ga bond. For the meaning of different lines, see text. Lower panel: Electronic structure factor, for (a) $S_c(\mathbf{k})$ and (b) $S_a(\mathbf{k})$. Note that of the two differ mainly around K^*, the true $S_c(\mathbf{k})$ being much larger.

c. Band structure and optical conductivity. Figure 3 shows the band structure of α-Ga. The strong anisotropy at the Fermi surface indicates preferential conduction along the planes, in agreement with the experiments. Details of the electronic structure at the Fermi level,[11] such as the small hole pocket in the k_y direction (barely visible on the scale of the picture), are well brought out. The presence of nearly parallel bonding-antibonding bands is typical of covalent materials. The gap (~ 2.3 eV) between these parallel bands, indicated by the arrows in Fig. 3, gives rise to a strong peak in the optical conductivity $\sigma(\omega)$ (Fig. 4). This is a rather unusual feature for a metallic system, and in fact directly reflects the bonding $\rightarrow$ antibonding transition of the Ga_2 "molecule." The agreement between the calculated and experimental $\sigma(\omega)$ (Ref. 12) is remarkably good, indicating that our first-principles theory correctly reproduces the electronic properties of α-Ga in considerable detail. The experimental shoulder at 1.5 eV is probably related to excitonic effects not included in our scheme.

d. Electronic-structure factor. Finally, we turn to the x-ray-related electronic-structure factor

$$S(\mathbf{k}) = \Omega^{-1}\int \rho(\mathbf{r})\exp(i\mathbf{k}\cdot\mathbf{r})d\mathbf{r}\,.$$

We have calculated $S(\mathbf{k})$ in two different ways: the first $[S_c(\mathbf{k})]$ using the true electronic charge density and the second $[S_a(\mathbf{k})]$ using a superposition of atomic charges. $S_c(\mathbf{k})$ and $S_a(\mathbf{k})$, shown in the lower panel of Fig. 5, show similar overall behavior, apart from a close multiplet K^* of reciprocal-lattice vectors ([113] [121] [022] [004]), whereas a much stronger contribution is present in $S_c(\mathbf{k})$. Figure 5 also shows the true total electron density along the Ga_2 bond A, the atomic superposition B, their difference C, and the charge obtained by Fourier synthesis of the K^* multiplet of the density D. The difference between C and D is small, indicating that the Ga_2 bond is indeed responsible for this behavior of the $S_c(\mathbf{k})$. Thus, we suggest that accurate x-ray-scattering experiments on α-Ga should directly reveal the presence of the molecular bonds.

In conclusion, we have shown that the LDA is capable of describing the subtle differences between the rather complicated structures of Ga. The physics of the α phase of Ga can be understood as being due to a remarkable coexistence of molecular and metallic behavior. It is proposed that accurate x-ray-scattering experiments could further prove this point.

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