Pressure-Driven "Molecular Metal" to "Atomic Metal" Transition in Crystalline Ga

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We present the ultrasonic study of gallium (Ga I) under high pressure up to 1.7 GPa, including the measurements of the density and elastic properties during phase transitions to Ga II and to a liquid state. The observed large drop of both bulk and shear moduli (by 30% and 55%, correspondingly) during the phase transition to Ga II, as well as the increase of the Poisson's ratio from typically "covalent" (≈0.22) to "metallic" (≈0.32) values, experimentally testifies to the coexistence of a molecular and metallic behavior in Ga I and to the disappearance of the "covalency" during the transition to Ga II. A high value of the pressure derivative of the bulk modulus for Ga I and the increase in the Poisson's ratio can be associated with the weakening of the covalency in compressed Ga I and considered as a precursor of the transition to normal metal.

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Elementary gallium has a great many unique properties as a substance. Low melting temperature and high boiling temperature of gallium at normal pressure account for an exceptionally wide stability range of liquid gallium (from 303 K to 2478 K). Single crystals of the stable phase Ga I show one of the highest thermal and electroconductivity anisotropies [1] among elementary metals. Unlike most metals, the melting of Ga I is accompanied by the density increase (≈3.2%) [2]. At atmospheric pressure, the Ga melt can be easily undercooled and conserved in the metastable state for months, which is impossible for any other metal. All these uncommon properties can be clearly related to the coexistence of a covalent and metallic bonding in Ga I [3–7].

At normal conditions Ga I has the base-centered orthorombic structure with eight atoms per unit cell (space group *Cmca*, $a = 4.5192$ Å, $b = 7.6586$ Å, and $c = 4.5258$ Å) [8]. Within the framework of the Ga I unit cell it is possible to set off conditionally the Ga_2 dimers ("molecules") with interatomic distance of 2.44 Å being the shortest among other atomic pairs. Each of the next three shells contains two atoms, which are 0.27 Å, 0.3 Å, and 0.39 Å further apart the first monoatomic shell. An alternative interpretation of the Ga I structure considers strongly buckled parallel planes connected by short bonds between the first neighbor atoms that lie in different planes. Electrical and thermal conductivity is much greater in the (010) buckled planes than along the [010] direction, to which the shortest Ga_2 dimers are angled quite close. Theoretical calculations suggest a strongly nonuniform distribution of the electron density in Ga I and the existence of the Ga_2 quasimolecules with a strong contribution of covalent interaction [3,5]. The force constant between the nearest neighbors in a Ga_2 quasimolecule is twice as strong as on average in the structure [3,5]. Experimentally, the existence of Ga_2 molecules in solid gallium was also verified by means of optic measurements [9], scanning tunneling microscopy [4], and surface x-ray diffraction [6].

Being stable at normal conditions, Ga I substance undergoes a number of phase transitions at high pressures (see the inset in Fig. 1). Depending on the pressure-temperature paths, Ga I can transform either to Ga II (a phase with a complex structure that can be recognized as distorted bcc) or (through the melt) to Ga III (bct), and at further compression to Ga IV (fcc), and Ga V (hR6) [10–15]. There are several known metastable forms of gallium [11]. The structures of high-pressure phases are typical for normal metals (taking into account the coordination numbers and a bond length), and one should expect a loss of pseudocovalency in gallium during the reconstruction of the quasimolecular structure of Ga I to a typical atomic metal under compression.

It is well known that the change of the bond type has an effect on all physical and chemical properties of a substance, among them the elastic characteristics which are very sensitive to the bond type and to the electronic density

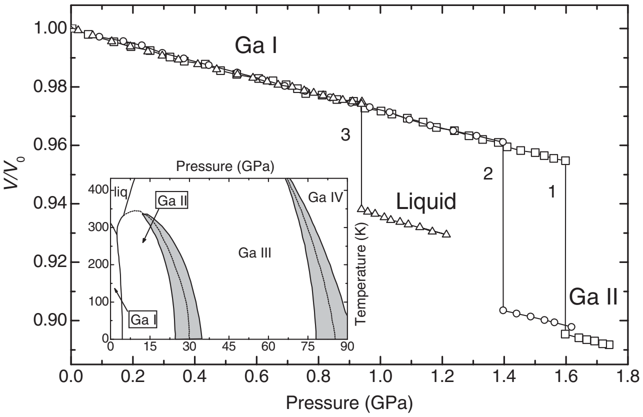

FIG. 1. The relative volume-versus-pressure dependencies for Ga at different temperatures. Curve 1 (□) is for $T = 247$ K, curve 2 (○) is for $T = 259.5$ K, and curve 3 (△) is for $T = 285$ K. The inset shows the pressure-temperature phase diagram of Ga from Ref. [10].

distribution in materials. Particularly, the bulk B and shear G moduli are mainly defined by the electron density as well as by the degree of space anisotropy of the electron density [16]. Usually the bulk modulus increases at phase transition to denser structures; however, in some rare cases of the network substances the decrease of the bulk modulus can occur [17]. The value of the shear modulus (or the G/B ratio) is more sensitive to a directional anisotropy of the electron density along the bonds. The electron density in turn directly related to a covalency degree. The G values for high-pressure phases are usually higher than those for low-pressure phases, although in the case of transitions accompanied by the decrease of covalency, the G value can go down [18–20]. In this respect the Poisson ratio [$\sigma = (3B - 2G)/(6B + 2G)$ for isotropic substance] can be considered as an indicator of the degree of covalency. For the pair central-forces interaction, $\sigma = 0.25$; for the majority of metals σ varied in the interval 0.3–0.45 (with the exception of Be), and for covalent substances σ varied in the interval 0.05–0.3 [16].

To our knowledge, the elastic properties of gallium have not been studied at high pressures previously, whereas the study of the pressure derivative of the bulk modulus for Ga I [10,21,22] has produced discrepant results. At the same time, the elastic properties, being a direct macroscopic manifestation of the microscopic interatomic forces, are very important for a deeper insight into the bonding nature of Ga I and for the verification of theoretical results [3,5,22]. In experiments, the molecular nature of Ga I was basically attested by the study of surface structure and electronic properties (see Refs. [1,4,6,9] and references therein). The inelastic neutron scattering [23] revealed that Ga I has high energy (as compared, e.g., with the highest frequency in the phonon spectrum of the metastable ordinary-metallic β-Ga [24]) optic phonon modes for all k vectors along the [010] direction associated with the preferable orientations of the Ga_2 molecules. Still, the study of gallium elasticity can provide experimental data on the contribution of metallic and covalent forces in Ga I under pressure. Particularly, one can expect considerable changes of the bulk and shear moduli, as well as of the Poisson's ratio, to occur during phase transition from "molecular" to "atomic" metal.

In this work we present the ultrasonic and volumetric study of Ga upon compression and heating, including Ga I, Ga II, and liquid phases. This study is the first to provide accurate data (including direct volume measurements) on the elastic characteristics of these phases under pressure and to present an exotic example of significant drop of both bulk and shear moduli with the increase in density during the Ga I–Ga II transition. As it seems, the obtained results can be of considerable importance in understanding the nature of other very rare examples of "molecular metals" like high-pressure phases of I_2, Br_2, and O_2 [25–27].

To obtain a homogeneous polycrystalline sample, a thin-walled duralumin capsule was filled with liquid gallium of 99.99% purity and then rapidly cooled in liquid nitrogen. The samples obtained were cylinders of 7–10 mm in height and 16 mm in diameter. The measurements were carried out using an ultrasonic piezometer at pressures up to 1.7 GPa in the temperature range 240–360 K in accordance with the procedure described in [28]. The travel time of an ultrasonic wave was directly measured (with an accuracy of 1 ns) by a MATEK equipment-based "Akustomer-1" device designed in the Institute for High Pressure Physics of the Russian Academy of Sciences. Quartz plates with a carrier frequency of 5 MHz were employed as piezogauges. The variations of the ultrasonic signal travel path were also measured to an accuracy of 0.005 mm by means of a displacement indicating gauge. The work resulted in deducing pressure and temperature dependencies of the longitudinal and transversal wave velocities and of the relative volume in gallium. We estimated the accuracy of determining the bulk and shear moduli as 1.5%. The excellent reproducibility of the experimental data both in the compression and decompres-

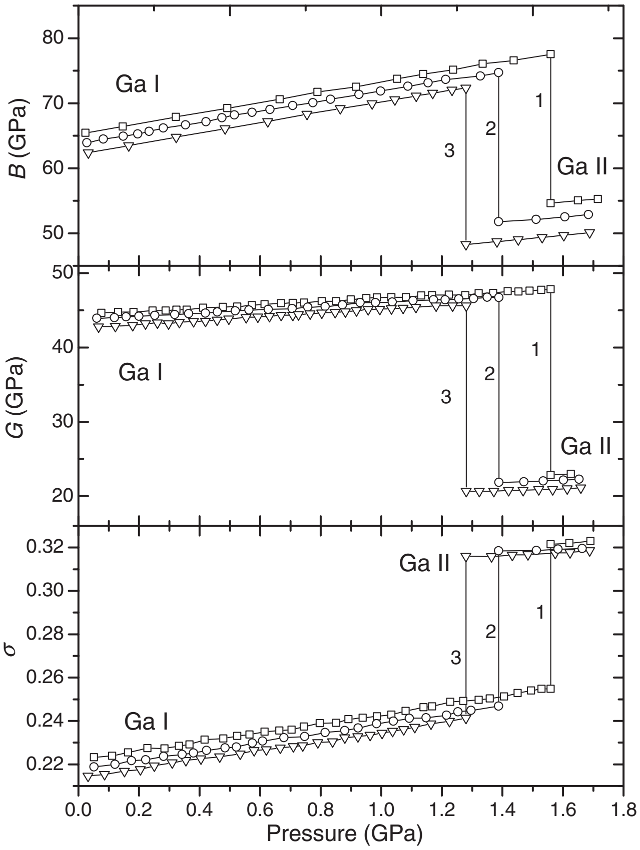

FIG. 2. Pressure dependencies of the bulk modulus (B), the shear modulus (G), and the Poisson's ratio (σ) of Ga at different temperatures. Curve 1 (□) is for $T = 247$ K, curve 2 (○) is for $T = 259.5$ K, and curve 3 (▽) is for $T = 268$ K.

sion cycles gives the evidence of the absence of significant texture in the gallium samples under investigation.

The typical pressure-versus-volume dependencies are presented in Fig. 1. Curve 3 shows the gallium compression including melting, whereas curves 1 and 2 correspond to the Ga I–Ga II transition. The values of the volume jumps (3.5% and 5.7%, correspondingly) are in good agreement with the results [29–31]. The pressure dependencies of the bulk and shear moduli are shown in Fig. 2. Both moduli for the Ga I phase have a linear pressure dependence without any pretransitional effects, although a strong decrease of the shear ultrasonic wave amplitude was detected. The B'_p value is rather large ($\approx$7.8–8.0), which does not agree with the data obtained in [21] and in the theoretical calculations [5,22], but does agree with the one estimated in [10]. The value $G'_p \approx 2.3$ is in agreement with the results [21]. The phase transition Ga I–Ga II manifests a large drop of both bulk ($\approx$30%) and shear moduli ($\approx$55%). Such behavior of the moduli is very unusual as it happens during the transition to a denser modification.

The value σ obtained for Ga I at atmospheric pressure ranging from $\approx$0.22 to $\approx$0.25 is typical for covalent substances (Fig. 2). The high-pressure phase Ga II is characterized by the pressure derivative of the bulk modulus $\approx$4.6–4.8 and the Poisson ratio $\sigma \approx 0.32$, which are typical for metals and implies a more isotropic electronic density in this phase. A large drop of B and even larger drop of G during the Ga I–Ga II transition mean a loss in the covalency. Up to date such significant drops of the shear modulus have been experimentally observed only in InSb and Bi [19,20]; according to the calculation data, they take place at the α-Sn-to-β-Sn phase transition [18]. The detected significant drop of the bulk modulus at phase transition has not been observed earlier for any metal.

The increase of the Poisson's ratio of Ga I with pressure (Fig. 2) agrees with the assumption that the covalency of gallium decreases with pressure. It is worth noting that this increase directly relates to a high value of the pressure derivative of the bulk modulus ($\approx$7.8–8), and there are no pretransitional effects (i.e., the changes of the pressure derivative of elastic characteristics) in the behavior of elasticity of Ga I up to the point of phase transition. Such behavior can be associated with specific features of electronic density and structure of Ga I. Indeed, although the (010) buckled planes are considered to be metallic ones, when a molecular structure of gallium is discussed, the electron density of the bonds forming the buckled planes is still quite anisotropic and yields to the electron density in the shortest Ga_2 dimers only by factor $\approx$1.5 [3,5]. So, the contribution of covalent bonding in Ga I has a three-dimensional nature that clarifies the high values of elastic moduli in Ga I with respect to normal metal Ga II having a more uniform distribution of electron density [3,5]. As it was pointed above, each atom in Ga I has 7 neighbors in the first 4 shells being array from the central atom by 2.44–2.83 Å. Thus, the lattice of Ga I is intermediate between the open packed structures with the first coordination numbers $n \leq 6$ and closed packed lattices of typical metals with $n \geq 8$. The substances with open packed structures tend to collapse under pressure and often demonstrate the negative derivatives of elastic constants as precursor of a lattice instability [32]. In this respect the fast increase of the bulk modulus in Ga I is a demonstration of the contribution of covalent bonding in nonopen packed structure that still tends to transit to more close packed normal metals Ga II or Ga III [33].

In the present work the ultrasonic measurements under pressure have proved to be of much promise for studying the changes of the nature of bonding in elementary gallium. We believe that the experimental and theoretical studies of the elastic characteristics of various substances under compression can give much more evidence of bond type changes in materials under pressure.

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