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A GALLIUM MULTIPHASE EQUATION OF STATE

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Abstract. A new SESAME multiphase Gallium equation of state (EOS) has been developed. The equation of state includes three of the solid phases (Ga I, Ga II, Ga III) and a fluid phase (liquid/gas). The EOS includes consistent latent heat between the phases. We compare the results to the liquid Hugoniot data. We also explore the possibility of re-freezing via dynamic means such as isentropic and shock compression.
Keywords: Gallium, Multi-Phase, Equation of State
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INTRODUCTION

Given its low melting point of 303 K, its anomalous melting curve (the melting temperature decreases with increasing pressure) and its numerous solid phases, Ga appears to be a very interesting material for studies of dynamic phase transitions. Gallium has five known equilibrium solid phases [1, 2] and exhibits strong metastability in some of its phase transitions[3]. In particular, the supercooled liquid phase is exceptionally long-lived. Due to the complexity of its phase diagram, Ga is an excellent test for the capabilities of our multiphase models and algorithms.

In this paper, we discuss the development of a multi-phase equation of state (EOS) for Ga. This EOS explicitly treats three solid phases and the fluid phase. Separate free energy functions are created for each phase, and a global equilibrium EOS is then generated by combining the phases, allowing for coexistence [4]. In this way, heats of transformation are included, and the Clausius-Clapeyron relation is satisfied. The resultant EOS is wide-ranging in that limiting behaviors for extreme high temperature and high compression are included in the models. Model parameters for the individual phases have been obtained empirically. The result is an EOS that is internally consistent and integrates a wide range of experimental data. Such an EOS is useful for planning dynamic experiments to probe phase changes. In particular, the EOS can be used to make predictions of the path of Hugoniots and isentropes through the phase diagram, and hydrodynamic anomalies, such as shock splitting. In this paper, we briefly describe the development of our Ga EOS, and show illustrative comparisons with data. We then give results for Hugoniots and isentropes from different initial states and their paths through the phase diagram. As a result of this work, we predict that low pressure shocks starting from the solid at STP will spontaneously spread into compression fans as the Ga I/liquid coexistence region is entered.

EOS MODEL

The Helmholtz free energy of each phase is taken to have a three-term decomposition, which consists of a cold curve, ion thermal, and electron thermal contribution. For all phases, the Thomas Fermi Dirac (TFD) model was used for the electron thermal term (the TFD cold energy is subtracted from the finite T TFD free energy). For the solid phases, the Debye model is used for the ion thermal term. Our liquid phase ion thermal model is based on relating the liquid to a solid phase [5, 6]. The liquid is assumed to have a specific heat $c_V = 3Nk_B$ near melting, and to have a volume-independent entropy off-

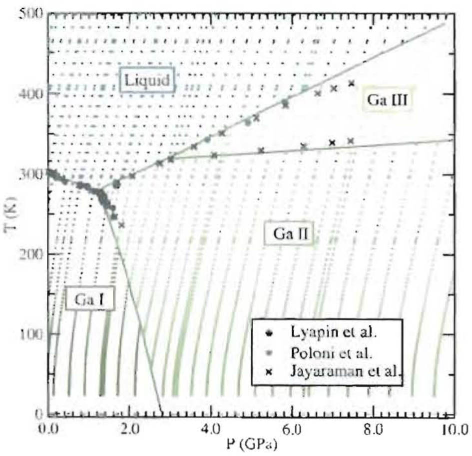

FIGURE 1. Phase diagram compared to the available data [14, 2, 3].

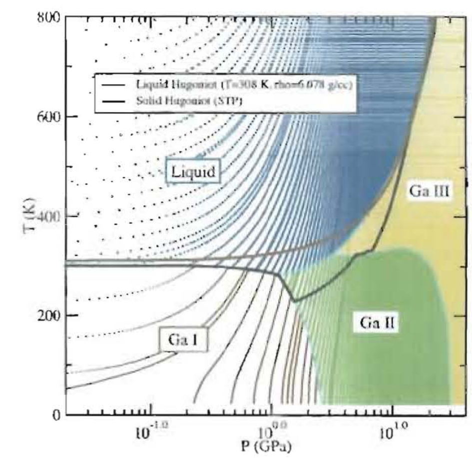

FIGURE 2. The top solid curve is the Hugoniot starting at 308K from the liquid state. The lower solid curve is the Hugoniot at STP conditions.

set ΔS_V with respect to the solid. An energy offset $\Delta\phi(V) = \Delta S_V T_{\mathrm{melt}}(V)$ determines the melting temperature. The function $T_{\mathrm{melt}}(V)$ is assumed to have a Lindemann form. At higher temperature, the excess, specific heat is assumed to fall off as a power law in $T/T_{\mathrm{melt}}(V)$, and finally, the liquid free energy merges smoothly into that of an ideal gas at very high temperature [7]. In the present case, the liquid is assumed to be related normally to the Ga II solid phase. This assumption is based on the picture that liquid Ga and Ga II are normal metals, while Ga I is an abnormal metal with low conductivity and partially covalent bonding [2]. In this picture, the anomalous melting results from the exceptional properties of the Ga I solid phase.

The phase diagram for gallium has been thoroughly summarized in the recent work of Lyapin et al. [2]. A first-principles study by Voloshina et al. [8] connects the various structures of Gallium to their electronic properties. The Ga I phase is orthorhombic and can be pictured as consisting of a periodic array of Ga_2 "quasi-molecules". Ga II was thought to have a bcc structure with 12 atoms per unit cell [9], but was recently reported to have an orthorhombic structure with 104 atoms per cell [10]. The Ga III phase is simple body-centered tetragonal [9]. The Ga IV phase, which is face-centered cubic, is related to Ga III by a continuous change of the unit cell with no volume change [11], and so is considered to be part of the Ga III phase for this EOS. The recently reported Ga V phase [10] was not included due to a lack of information about it. The cold curve for the Ga III phase is smoothly merged into the TFD cold curve at ultra high pressure.

In evaluating the parameters for the individual phases, we have used ambient pressure thermophysical data [12, 13], Hugoniot data [15, 16], the measured phase diagram [2, 14, 3], diamond anvil cell data [1], measured volume changes, and the bulk moduli of the Ga I, II, and liquid phases under pressure [2]. As an illustration of the relation between data and model parameters, we note that the volume changes are primarily controlled by the cold curve, while phase boundary slopes, together with volume changes, determine the entropy changes, which determine the Debye temperatures. Because the relation between data and model parameters is not one to one, we adopt an iterative procedure. Initial parameter estimates are made based on approximate relations, then these estimates are refined by graphical comparison of the EOS with data.

Figure 1 compares the calculated boundaries to the available data [14, 2, 3]. As illustrated in the figure, the liquid model simultaneously reproduces the anomalous melting behavior between the Ga I and liquid phases, and the normal melting behavior for the higher pressure phases. This agreement lends

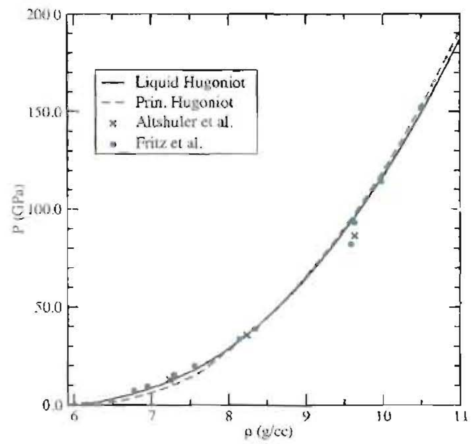

FIGURE 3. The dashed curve is the principal Hugoniot, The solid curve is the liquid Hugoniot at $308K$ and is compared to the experiment [15, 16].

support to our model assumption that the liquid is normal in relation to the Ga II phase. The exceptionally large entropy change $\Delta S_V = 2.37Nk_B$ [12] for the Ga I/liquid transition at 1 atm is imposed through the parameters of the liquid EOS. The physical mechanism for this anomaly (typical values are $\Delta S_V \approx 0.8Nk_B$) is unknown. Capturing the Ga II/Ga III phase boundary involved a particularly sensitive parameter study which resulted in a very useful constraint on the Ga III bulk modulus.

PREDICTIONS FOR DYNAMIC COMPRESSION

Studying dynamic loading of Gallium experimentally at different initial temperatures either by shock or isentropic compression should yield interesting results. We illustrate via Figure 2 the complex path that the Hugoniot initiated from the solid state follows. The figure shows the Hugoniot curves in the T,P plane, along with the phase diagram, for initial states at STP in the Ga I phase, and in the liquid at 308 K, as in the experiments of Fritz and Carter [15]. The solid Hugoniot quickly enters into the Ga I/Liquid two-phase region and then continues along the Ga I/Ga II phase boundary. Figure 2 shows the same two Hugoniot curves in the P,ρ plane along with data [15, 16]. At low pressures, where it follows the Ga I/liquid phase boundary, the solid Hugoniot is concave downward in pressure-volume space. Thus, we predict that shock waves in this pressure range are unstable with respect to spontaneously spreading into isentropic compression fans. This is very unusual behavior, and results from the anomalous decrease in the bulk modulus with increasing density in going from Ga I to liquid [2]. We predict complete melting under shock from STP at approximately 870 K and 25.7 GPa. By cooling the to below 270 K, the Ga I/liquid two phase region can be avoided, and the Ga I/Ga II transition is the first one encountered. As a result of cooling the sample, the EOS predicts approximately a 200 K and 5 GPa increase in the melt temperature and pressure. We expect the Ga II/Ga III phase transition will be difficult to measure due to the small density difference of 0.3%. Sound velocities measurements would be extremely useful along with the shock data covering these phase transitions. Note that the liquid Hugoniot enters into the liquid/Ga III two phase region but does not transition into pure solid.

Figure 4 is a comparison of four different isentropes, two initialized in the liquid state and two from the solid. With only a 2 degree temperature differences in each set, one can clearly see the substantial difference in the loading paths. Performing isentropic experiments will play a key roll in validating the phase boundaries. It is interesting to see that one of the liquid and one of the solid isentropes followed the same path along the Ga II/ liquid phase boundary and then deviated at the triple point.

Because the supercooled liquid state is long lived, it is possible to shock from this state. To simulated these conditions, we have generated an EOS with the Ga I phase taken out. This allows the liquid to be stable down to $T \approx 260$ K. Figure 5 shows the phase diagram for this model along with the Hugoniot from an initial liquid state at $T = 280$ K. As in all cases we studied, the Hugoniot enters a mixed solid/liquid region, but then moves of into pure liquid.

CONCLUSIONS

In summary, we have generated a wide-range, empirical EOS for Ga that includes three solid phases and a fluid phase. Using this EOS, we make predictions concerning dynamic loading paths. We find

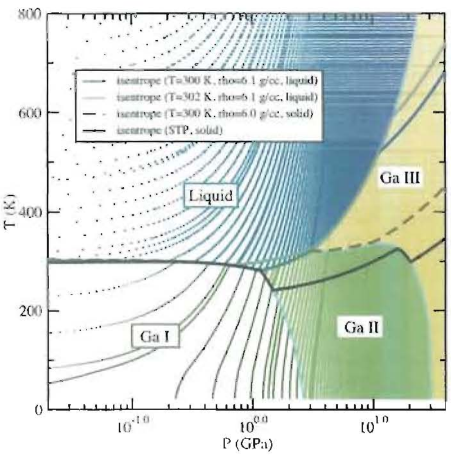

FIGURE 4. The curves represent different isentropes sampling different phase space.

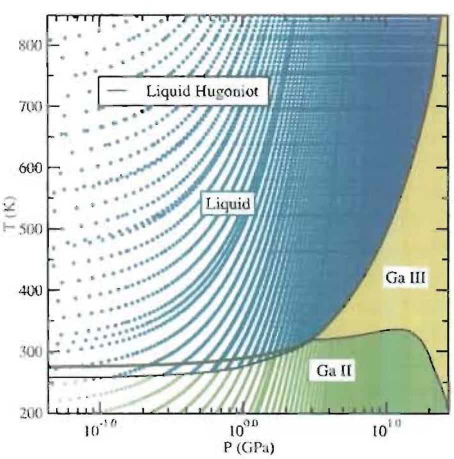

FIGURE 5. Hugoniot for intial state in supercooled liquid. This is modeled here by removing the Ga I phase, allowing the liquid to be stable at lower temperature.

complex behavior for these paths. For instance, the principal Hugoniot partially melts, then enters a region of mixed solid phases. We predict that this partial melting leads to spontaneous spreading of shock waves at low pressure, due to the unusual behavior of the bulk modulus in this region.

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