Resistivity and equation of state of warmed gallium melt in megabar pressure

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Abstract. The electrical conductivity of gallium melt was measured under multiple-shock compression up to ≈100 GPa. The semi-empirical equations of state (EOS) are constructed in the shock pressure range 30-300 GPa. The EOS were used for reconstruction of the thermodynamic history of the sample in the experiments and for the subsequent definition of the volume-temperature dependence of gallium melt resistivity. It was shown that the volume-temperature dependence of gallium melt is proportional to temperature and inversely to the square of characteristic temperature in the shock pressure range 30-80 GPa and temperatures of 1000-2000 K. Thus warmed high pressure gallium phase melt possesses metal conductivity.

1. Introduction
As is well known, under normal conditions crystalline gallium is quasimolecular crystals with high electrical resistance. Upon melting, the resistance of gallium is halved, and the melt becomes liquid metal (see [1]). At the same time, according to theoretical work [2], in gallium melt, along with a metallic type of interaction, the existence is also possible of joint covalent dimers Ga_2, remaining from the quasi-molecular phase of crystalline gallium.

According to [2], the concentration of dimers in the gallium melt depends on temperature and pressure, and it can be assumed that increasing the concentration of gallium atoms covalently bonded in a highly compressed and heated melt will change its conductivity. In our study, the measurement of the electrical conductivity of the shock-gallium melt using the technique described in [3,4] was executed. The purpose of the work was to define the value and character of the electrical conductivity of the gallium melt under megabar pressure shock compression.

2. Method and results
Crystalline gallium in the form of granules of 5-10 mm and a purity of 99.99% was acquired from the catalog company Aldrich (№ 263265-10G). A thin ribbon manufactured from the granules was used to prepare samples. Granules were pressed between two muscovite plates with a hydraulic press up to pressure 0.5 GPa at temperatures 290 K. The granules melted and turned into the thin foil. Then the pressure is continuously decreased and the sample solidified, remaining in the form of a thin (0.05 mm) foil. The ribbon-sample was produced from this foil. Experiments were performed in the traditional way to measure the electrical resistance of the prepared sample during multiple shock compression (see [3,4]).

The measuring cell is shown in the figure 1. The sample 1 was shunted by the manganin gauge 2. This parallel connect had common conductor of current 3 made of a copper foil 20 microns in
thickness. Symmetrically located to the shunt sensor was a “clean” manganin gauge 4. Parts 1-4 were located between two muscovite mica plates 5 with a thickness of 80-100 microns. Air gaps between the muscovite mica plates and sensors were replaced with the help of a high-vacuum leak sealant 6. The impactor velocity $W_0$ at the moment of collision with the target was $W_0 = 2.6$ km/s.

**Figure 1.** The experimental setup to measure the electrical conductivity of the samples under multiple shock compression. Dashed rectangle denotes the measuring cell. 1 is a sample, 2 is the manganin shunt, 3 is the copper foil, 4 is the manganin gauge. 5 is a muscovite mica plate, 6 is the high-vacuum leak sealant, 7 is the Teflon film, 8 is the stainless steel (304 type) plate thickness 2.5 mm and 4.92 mm, 9 is the steel impactor thickness 3.5 mm, 10 is an explosive, 11 is an explosive lens.

**Figure 2.** Experimental profile of resistivity (1) and calculated profiles of pressure (2), temperature (3) and volume (4).

The electrical conductivity of the sample was measured using a bridge circuit. During loading across the sample 1, shunt 2 and manganin gauge 4 DC currents $J_{01} = J_{02} = 9.9$ A were passed from the two independent switching power supplies. In the experiment the profiles (depending on the time $t$) of the voltage unbalance of the bridge $\Delta U = \Delta U(t)$ were measured. Resistivity profiles were defined as $R_1(t) = R_{01} + k_1 \Delta U_1$ for the shunted sample 1-2, and $R_2(t) = R_{02} + k_2 \Delta U_2$ for the manganin gauge 4,
where $k_1$ and $k_2$ were the pre-determined calibration coefficients. The profile of the sample resistivity $R = R(t)$ was calculated as the difference between the profiles of $R_1(t)$ and $R_2(t)$. The initial resistance of the samples of gallium was $R_0 = 0.3 - 0.7$ $\Omega$. A typical experimental profile of $R(t)$ is shown in graph 1 in figure 2a.

In analyzing the loading history of the gallium sample, the manganin gauge served only as a timer to “anchor” the calculated pressure profiles $P = P(t)$, the temperature $T = T(t)$ and the volume $V = V(t)$ with the experimental profile $R = R(t)$ electrical resistivity of the shocked gallium sample.

Calculation of the thermodynamic history of the sample was carried out in the framework of a one-dimensional hydrocode, granted by V.V. Kim. To close the system of the Euler equations of conservation, our own semi-empirical equations of state were used in the form of [4]. The semi-empirical equation of state of gallium melt is presented in the Appendix A. The calculated profiles of $P$, $T$, $V$ in a sample of gallium are shown in graphs 2, 3 and 4 in figure 2b.

The profile of the electrical resistivity $\rho(t)$ is calculated as $\rho(t) = \rho_0 R(t) V(t) / R_0 V_0$ where $\rho_0 = 0.4$ $\mu\Omega$m, $V_0 = 11.44$ cm$^3$/mole. The bold profile 1 (see figure 2) is the experimental oscillograme which has been smoothed. The i-points are placed on this profile by hand through 0.1 mcs. The calculated pressures $P_i$ from profile 2, temperatures $T_i$ from profile 3 and volumes $V_i$ from profile were connected with each i-point. Then the resistivity $\rho_i(T_i, P_i)$ have been calculated as a function $\rho_i(T_i, P_i)$. The set of $\rho_i(T_i, P_i)$ points are shown on figure 3. So the figure 3 shows the trajectory of the electrical resistivity of gallium in the coordinates $\{\rho, P, T\}$.

3. Discussion
In the plane $P$, $T$ of figure 3, the data [5] are presented for the melting pressure phases of gallium in the shock wave. According to [5], the region of the mixture of solid and liquid phase extends up to 50 GPa. Our multiple shock experiments the phase trajectory is replaced over [5] data (see figure 6 in Appendix A). Furthermore, the calculated high pressure isotherm of liquid Ga coincide with experimental data [8] (see insert on figure 6) at pressure ~ 1 GPa. Therefore, we can say that in our multiple shock experiments the gallium was in a molten state at pressures greater than 50 GPa and up to 1 GPa in unloading.

Figure 3. Pressure-temperature dependence of the electrical resistivity $\rho$ (top line), gallium melt at pressures $P$ up to 80 GPa and temperatures up to 2000 K. The bottom line in the plane of $T$, $P$ - phase trajectory of the loading and unloading of the sample under stepwise shock loading. Arrows indicate the path of loading and unloading. Square in the plane $P$,$T$ - data from reference [5].
It can be seen (figure 3) that in the compression phase, with increasing pressure and temperature, the resistivity of the gallium melt decreases. Then there is an increase in electrical resistance in the compression phase. This behavior can be qualitatively interpreted by two mechanisms. First, it may indicate the suppression of dimers with increasing pressure, and their generation with decreasing pressure at high residual temperatures. The second mechanism is the body-temperature dependence of the resistivity of a material having a metal conductivity.

Our quantitative evaluation of the evidence favors the second mechanism. Indeed, according to the Bloch-Gruneneisen formula, the resistivity of the metal is proportional to the temperature $T$ and inversely proportional to the square of the characteristic temperature $\Theta$, i.e. $\rho \sim T / \Theta^2$. Given that $\Theta$ depends on $\Theta = \Theta(V)$, it can be said that the temperature dependence of the volumetric resistivity of the metal can be represented as a straight line for coordinates $\{\rho; x\}$ where $x = T / \Theta^2$.

Figure 4 presents the data from figure 3 in the coordinates $\{\rho; x\}$, where, for $\Theta = \Theta(V)$ a functional dependence is adopted in the form of equation (A.2) (see Appendix A).

As can be seen, the volume-temperature dependence of the resistivity of the gallium melt can be represented as

$$\rho = \rho_m + \alpha_m \frac{T}{\Theta^2} = \rho_m + \alpha_m z, \quad z = \frac{T}{\Theta^2} \left( \frac{\nu_0 - V_0}{\nu_0 - V} \right)^{4/3} \left( \frac{V}{V_0} \right)^{4/3}. \quad (1)$$

According to equation (1), the temperature coefficient of the resistivity $\alpha$ of gallium melt depends on temperature and volume as follows:

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT} = \frac{\alpha_m}{\rho_m \Theta^2 + \alpha_m T}. \quad (2)$$

Equation (2) gives a reasonable value of the temperature coefficient of resistivity $\alpha$ at zero pressure

$$\alpha = \frac{1}{\rho} \frac{d\rho}{dT} = \frac{\alpha_m}{\rho_m \Theta^2 + \alpha_m T} \bigg|_{V_0, T_0} = (2.5(\pm0.15)) \times 10^{-3} \, 1/K. \quad (3)$$

The value $\alpha$ for the Ga melt coincides with the value of reference data from [1].

Let us consider the value of errors on figure 4. Our EOS agree with data [6,7] with accuracy 2% (see figure 5). But the resistivity error is a lot more. The error in resistivity was determined from the measurement error in resistance and the uncertainty of the $T$ and $V$, arising when smoothing the profile 1. We have adopted this accumulated error of 10 per cent for both $\rho$ and the $x$. 

Figure 4. Volume-temperature dependence of the electrical resistivity $\rho = \rho(V, T)$ of gallium melt in coordinates $\{\rho; x\}$. Line 1 is drawn by the least squares method.
4. Conclusions
Thus, the analysis of the phase trajectories \{\rho, V, T\} shows that the volume-temperature dependence \(\rho = \rho(V, T)\) of gallium melt at pressures between 30-80 GPa and temperatures of 1000-2000 K is directly proportional to temperature and inversely proportional to the square of the characteristic temperature \(\rho \sim T / \Theta^2\). This dependence \(\rho = \rho(V, T)\) means that the high pressure phase of gallium melt at megabar pressures and thousand-degree temperatures has metallic conductivity. Within the limits of measurement accuracy, it can be assumed that the concentration of “molecular pairs” in such melt is negligible.

Appendix A. Equations of state.
The semi-empirical approach for the phonon part of the free energy of the melt, \(F = F(V, T; \nu_x)\), where \(V\) is the specific volume of the material, \(T\) is the temperature, \(\nu_x\) is the fitting parameter, is based on the model of Einstein oscillators
\[
F = 3R \left[ \Theta \left( \frac{2}{T} \right) + T \ln \left(1 - \exp \left(-\frac{T}{\Theta}\right)\right)\right] + RT + E_x. \tag{A.1}
\]
Where
\[
\Theta = \Theta_0 \left(\frac{\nu_0 - V}{\nu_0 - V_0} \left(\frac{V_0}{V}\right)^{2/3}\right), \tag{A.2}
\]
\[
\nu_0 = V_0 \left(1 + \frac{2}{\gamma_0 - 2/3}\right). \tag{A.3}
\]
In (A.1) - (A.3) \(R\) is the specific gas constant, \(\gamma_0 = \gamma_0(V_0, T_0)\) is initial Gruneisen parameter, \(V_0\) is the initial volume, \(T_0\) is the initial temperature, \(E_x\) is the potential energy,
\[
E_x = -\nu_x (C_1 H_x + C_2 x + C_3), \tag{A.4}
\]
\[
H_x = 9 \left\{ \frac{1}{10} x^{10} + \frac{1}{2} x^8 + \frac{3}{7} x^6 - \frac{4}{7} x^5 - \frac{1}{7} x^7 + \frac{10}{70} x^{10} \right\}, \quad x = \frac{V}{\nu_x}. \tag{A.5}
\]
In (A.4) - (A.5) the \(C_1, C_2, C_3\) are constants expressed in terms of reference material properties and \(\nu_x\) (as mentioned above) is the fitting parameter. The value \(\nu_x\) was fitted so that calculation of Hugoniot and experimental of liquid Ga Hugoniots from [6,7] are coincident (see figure 5).

\[\textbf{Figure 5.}\] Experimental Hugoniot (points) and our simulation of Ga in D(shock velocity)-u(mass velocity) coordinates.
The thermal equation of state has the form \( P = P(V, T, \nu_x) = \left( \frac{\partial F}{\partial V} \right) \). The caloric equation of state has the form \( E = E(V, T, \nu_x) = F - T \left( \frac{\partial F}{\partial T} \right) \). Table 1 shows the parameters of (A.1)-(A.5) for shock compression gallium melt in the pressure range 30-300 GPa.

**Table 1.** The parameters for the phonon free energy of gallium melt [equation (A.1)].

| \( T_0 \) | \( V_0 \) | \( \Theta_0 \) | \( v_0 \) | \( \nu_x \) | \( C_1 \) | \( C_2 \) | \( C_3 \) |
|---|---|---|---|---|---|---|---|
| 303.0 | 11.44 | 189.0 | 37.942 | 18.304 | -637.664 | 13277.948 | -1744.014 |

Figure 6 shows the plane \( P - T \) estimates for the melting and phase mixture of [5]. From comparison of the data [5] with our calculated trajectories, we can conclude that in our experiments the samples of gallium were in a molten state under high pressure, starting with a pressure of 50 GPa and a temperature of 2000 K.

We emphasize that the high pressure isotherm \( P = P(V, T_0, \nu_x) \) with \( T_0 = 285 \) K is coincide with experiment [8] in pressure range 0-1.5 GPa (see the insert on figure 6). So we can say that our equation of state is realistic up to \( \sim 1 \) GPa.

**References**

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