Study of near-critical states of liquid–vapor phase transition of magnesium

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Abstract. Study of thermodynamic parameters of magnesium in the near-critical point region of the liquid–vapor phase transition and in the region of metal–nonmetal transition was carried out. Measurements of the electrical resistance of magnesium after shock compression and expansion into gas (helium) environment in the process of isobaric heating was carried out. Heating of the magnesium surface by heat transfer with hot helium was performed. The registered electrical resistance of expanded magnesium was about $10^4 - 10^5$ times lower than the electrical resistance of the magnesium under normal condition at the density less than the density of the critical point. Thus, metal–nonmetal transition was found in magnesium.

1. Introduction
Thermodynamic parameters in the critical point of liquid–vapor phase transition are used for construction of wide-range semiempirical equations of state. Near the critical point, two different metallic phases (liquid and gaseous metals) can be simultaneously. Possibility of this situation was predicted by Zel’’dovich and Landau [1], and according to modern data one seems widespread in metals [2]. To obtain reliable information about the critical point of liquid–vapor phase transition the metal–nonmetal transition for expanded metals should be investigated, since the critical point of liquid–vapor phase transition and region of dielectrization of expanded metals have close thermodynamic parameters. Dielectrization of expanded metals can take place at the expansion of gaseous metals to a density several times lower density of the molten metals [1–3]. The metal–nonmetal transition was experimentally investigated for limited number of expanded metals. These is cesium, rubidium and mercury [4]. For other metals, theoretical works [5, 6] or limited number of works on electric explosion of wires and metal foils [7, 8] are presented. The question under what parameters (density, pressure and temperature) of expanded metals there is metal–nonmetal transition relatively of the critical point parameters of the liquid–vapor phase transition is still not clear. The metal–nonmetal transition in mercury occurs at densities greater than the density of the critical point of the liquid–vapor phase transition [4]. For alkali metals it is assumed that the transition metal–nonmetal coincides with the phase transition liquid–vapor [6]. For tungsten, copper, aluminum the density of the metal–nonmetal transition is 5–15 times smaller than the normal density of the molten metal [7, 8].

In [5] estimates of the density of the critical point of the liquid–vapor phase transition and the density of the metal–nonmetal transition were made for a number of metals. For magnesium
density estimates of the critical point ($\rho_c = 0.35–0.56 \text{ g/cm}^3$) and the density of the phase transition metal–insulator ($\rho_{th} = 0.418 \text{ g/cm}^3$) are close.

In this work, study of thermodynamic parameters (temperature and pressure) of magnesium in the critical point region of the liquid–vapor phase transition and metal–nonmetal transition was carried out. The experimental assembly and method of producing near critical states magnesium are described in [9]. As compared with the experiments carried out in [9] in addition to measuring the intensity of the radiation measuring the electrical conductivity of expanded magnesium were performed. To measure the electrical conductivity of the expanded samples of magnesium two pairs of electrodes (figure 1) were introduced in experimental assembly. Measurements of the electrical conductivity of magnesium after shock compression and expansion in gas (helium) environment in the process of isobaric heating were carried out. Heating of magnesium surface was done by heat transfer with hot helium.

2. Experimental technique

The samples of magnesium of normal density were used for experiments. Samples in the form of discs of ~ 1 mm thickness and ~ 15 mm diameter were made and then compressed in a press between carbide plates having a polished surface to a thickness of ~ 0.7–0.3 mm. The scheme of the experimental assembly is presented in figure 1.

The samples placed on the steel bottom of the experimental assembly were shocked by the impact of a steel striker flying with a velocity ~ 5 km/s up to a pressure of 55 GPa. The investigated samples after shock compression expanded in helium medium with different initial pressure (1–40 bar). The shock wave velocity of helium was measured by the optical base length technique [10]. The particle velocity and pressure of expansion were calculated, using a helium equation of state [11] (chemical plasma model). Optical emission from sample was observed with a multichannel optical pyrometer. The magnesium sample at the shock compression is not heated under boiling temperature. For sample heating to the boiling temperature a process of heating of the metal by shock-compressed helium [9] was used.

The assembly for determining the electrical conductivity of magnesium (figure 1) consists of two pairs of electrodes made of steel wire (diameter ~ 1 mm), mounted on the bottom of the assembly around a window through which registration of optical radiation from the sample surface was carried out. The first pair of electrodes located at a distance ~ 3 mm from the sample surface, and the second pair of electrodes at the distance ~ 8 mm from the surface of the sample, each pair of electrodes is shunted with (~ 1–16 Ω) resistor. To measure the electrical resistance of sample bridge circuit was used [12]. During the measurement a constant current of 9.5 A from a pulsed current source was passed through the sample. The time profile of the bridge unbalancing $\Delta U(t)$ was registered. Resistance profiles were defined as $R(t) = K(\Delta U)$, where $K$ is a pre-determined calibration function. Typical experimental recordings $\delta = R(t)/R_0$ ($R_0$—initial sample resistance) are shown on figure 2. Measurement of the interaction time of the sample with the electrodes allows to determine the particle velocity and measurement of the time interval between the points $a$ and $b$ ($\Delta t = t_b - t_a$) allows to estimate the expanded sample thickness and density.

3. The results of measurement

Experimental recording of resistivity versus time in figures 2a (0.08 GPa) and 2b (0.16 GPa) for the different electrodes located closer and farther away from the sample are presented. For pressures below the critical point pressure (~ 0.08 GPa) on the electrodes located closer to the sample (1) a drop of the resistivity of the sample at the contact with the electrodes takes place, i.e. magnesium resistivity less electrical resistance of the shunt. At recording of the electrical resistance on the other pair of electrodes (2) the region of drop of the electrical resistance precedes the region in which decrease of the resistance of the sample according to linear law
Figure 1. Scheme of the experimental assembly for study of thermodynamic parameters (temperature and pressure) of the magnesium after shock compression and expansion in the helium environment and of the electrical conductivity by means of two pairs of electrodes disposed at different distances from the surface of the sample.

takes place. For pressures near the critical point (figure 2b) on both electrodes, reducing of the resistance observed before sharp drop of resistance (to register this region on the electrical resistance curves resistance of shunt was increased up to 10 times until 16 Ω). Probably at the higher initial pressure of helium more rapid heating of magnesium takes place as the heat transfer between magnesium and helium occurs by convective mixing.

The free surface of the magnesium in contact with hot helium (due to the high velocity of the shock wave the helium temperature (∼8000–10000 K) [11] is higher than temperature of the shock-compressed magnesium) undergoes isobaric heating and expansion. Recorded radiation intensity after reforming gives values of temperature ∼8000–10000 K. This temperature is close to the temperature obtained by calculation with helium state equation [11]. While stirring of the magnesium with helium emitting layer close to the temperature of helium occurs. Screening of the radiation from the sample surface due to radiation boundary layer of helium mixed with magnesium does not enable to measure the temperature of the dielectric state of magnesium. In the experiments measuring of the electrical resistance of the expanding magnesium, it was recorded that the electrical resistance of the dielectric magnesium grows with increasing pressure, and with decreasing density (figure 2c).

It is known that emission spectrum of mercury [2, 13] are varied at the metal–nonmetal transition, the low frequency radiation of mercury in the insulating state becomes transparent. Since the heating and expansion of magnesium in these experiments begins from the surface, when the density on the free surface reaches a value at which the metal–nonmetal transition takes place (metal-insulator transition in magnesium occurs at densities (0.42 g/cm³) below the critical point density (0.55 g/cm³) [14, 15]), the emission layer having a temperature and the emission spectrum different from the ones inside of the sample is formed.

If the emission spectrum of a dielectric layer of magnesium has the same character as in mercury, it is possible to assume that radiation is detected with the conductive and dielectric layers. At low frequencies of the radiation temperature of the conductive magnesium (dielectric
layer of magnesium is transparent) is recorded. At high frequency of radiation of the dielectric layer of magnesium is recorded. Indeed, in experiments with isobaric heating of magnesium it has been found that at pressures close to the critical point, the different brightness temperatures for various wavelengths were observed (figure 3).

The brightness temperature recorded at a wavelength of 600 nm is higher than brightness temperatures recorded at the lower frequencies of radiation. It can be assumed that the brightness temperature at a wavelength of 600 nm refers to a dielectric phase of magnesium and one at the wavelength of 1500 nm refers to a conductive phase.

Figure 4 shows the $P-T$ (pressure–temperature) diagram of magnesium at the near the critical point region of the liquid–vapor phase transition.

The dependence of the brightness temperature versus the pressure at the near critical point region at the wavelength of 1500 nm is in good agreement with the binodal and spinodal obtained from an equation of state [14, 15]. If the brightness temperature at a wavelength 600 nm refers to the dielectric phase of magnesium, then using a real gas equation of state ($P V/RT = Z$), and assuming that $Z$ is constant for the dielectric and conductive phase, we can estimate the density of the insulating phase (at the temperature 5000 K density $\sim 0.44$ g/cm$^3$; at a temperature of 6000 K density 0.37 g/cm$^3$). The estimates are close to the estimates of the density of the metal–nonmetal transition of magnesium, obtained in [5].

At the $P-T$ diagram there is a singularity at the pressure 0.24 ± 0.02 GPa. This the pressure coincides with estimation of critical point pressure obtained in [15]. Estimation of the temperature of the critical point of magnesium is obtained by linear extrapolating of the dependence of brightness temperature of magnesium (wavelength 1500 nm) (7—figure 4) at 0.24 GPa. The resulting estimate of the critical point temperature of magnesium is: $T_c = 4100 ± 300$ K.

![Figure 2](image-url)

**Figure 2.** A (0.08 GPa) and B (0.16 GPa)—the experimental data of the relative electrical conductivity; 1—electrodes are located at a distance of 3 mm from the sample and the 2—electrodes are located at a distance of 8 mm from the sample; 3, 4—recording of the brightness temperature converted from experimental radiation intensity. C—the dependence of electrical conductivity on the density for expanded magnesium.
Figure 3. Typical experimental snapshot of magnesium at the different wavelengths. Emission intensity already converted to brightness temperature.

Figure 4. Estimation of the critical point parameters of magnesium: 1—brightness temperature of magnesium in point b on the experimental snapshot of magnesium figure 3 (wavelength 1500 nm), 2—brightness temperature of magnesium in point a (wavelength 1500 nm, figure 3), 3—the brightness temperature of magnesium (wavelength 600 nm), 4–5—binodal and spinodal of magnesium [15], 6–7—linear interpolation of points (1) and (2).

4. Conclusions
(i) At the isobaric heating of magnesium at the near critical point region of the liquid–vapor phase transition the electrical conductivity of magnesium was registered, which is $10^4$–$10^5$
times lower than the electrical conductivity of magnesium under normal conditions (figure 2c).

(ii) Magnesium loses electrical conductivity at the expansion down to density less than density of the magnesium at the near critical point region.

(iii) The estimation of the critical point parameters of magnesium: $T_c = 4100 \pm 300$ K, $P_c = 0.24 \pm 0.02$ GPa.

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References
[1] Landau L D and Zeldovich Y B 1944 Sov. Phys. JETP 14 32–34
[2] Likalter A A 1992 Sov. Phys. Usp. 35 591–605
[3] Norman G A and Starostin A N 1970 Teplofiz. Vys. Temp. 8 413–438
[4] Hensel F 1989 Phys. Scr. 25 283–289
[5] Hess H, Schneidenbach H and Kloss A 1999 Int. J. Phys. Chem. Liq. 37 719–733
[6] Khomkin A L and Shumikhin A S 2014 JETP 118 72–79
[7] Rakhe A D, Korobenko V N, Savvatimski A I and Fortov V E 2004 Int. J. Thermophys. 25 1203–1214
[8] DeSilva A W and Rakhe A D 2005 Int. J. Thermophys. 26 1137–1149
[9] Emelyanov A N, Nikolaev D N, Pyalling A A and Ternovoi V Y 2008 Russ. J. Phys. Chem. B 2 637–642
[10] Emelyanov A N, Pyalling A A and Ternovoi V Y 2005 Int. J. Thermophys. 26 1985–1995
[11] Gryaznov V K 2000 Introductory Volume (Encyclopedia of Low-Temperature Plasma vol 1) ed Fortov V E (Moscow: Nauka)
[12] Golyshev A A and Molodets A M 2013 Combust. Explos. Shock Waves 49 219–224
[13] Ikezi H, Schwarzenegger K, Simons A L et al. 1978 Phys. Rev. B 18 2498–2505
[14] Fortov V E, Khishchenko K V, Levashov P R and Lomonosov I V 1998 Nucl. Instr. Meth. Phys. Res. A 415 604–608
[15] Lomonosov I V 2000 D.Sc. thesis Institute of Problems of Chemical Physics RAS, Chernogolovka