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Equation of state and conductivity of aluminum dense vapor plasma

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Introduction. State of the metals changed from the solid to gaseous state when the wire or foil samples rapidly heated by a current pulse. Near the critical temperatures there is occurs metal-nonmetal transition. Thermodynamic and transport properties are changed significantly. Many experiments and theoretical papers are devoted to investigation of features of metal-nonmetal transition. The pressure, internal energy and electrical conductivity are measured for rapid heated metal wires and foils [1, 2]. Theoretical papers might be separated conventionally on two groups. In the first group, the approaches developed in the theory of liquid metals are used for the subsequent extrapolation in the gas-plasma region [3]. The second group of papers are focused on a dense gas-plasma mixture and extrapolates calculations in near-critical region of liquid metals parameters [4]. Of course, that the first group of papers are well calculate properties of melting metals and badly describe transition in gas-plasma state of the evaporated metal. The second group of papers have the basic difficulties to describe the high density state, especially at low temperatures ($T \leq 10000\ K$). In the present study, which can be referred to the second group, for advance in the region of low temperatures and high densities the chemical model of aluminum vapor plasma for calculation of caloric (isochoric dependence of pressure P on internal energy E) and thermal (isothermal dependence of pressure on density) equations of state (EOS) is offered. In addition to electrons, atoms and various ion species A^{l+} where l = 1, 2, 3 considered in paper [4], we added molecules and molecular ions of aluminum. We used another than in [4] expressions to take into account the interaction of free charges in multiply charged plasma [5] and approach of Likalter [6] to take into account the ion-atom interaction. Dependence of a resistivity of plasma on internal energy calculated using Frost's interpolation formula and our caloric EOS. The satisfactory agreement with experimental data is received and the important role of molecules and molecular ions of aluminum in an initial phase of heating is shown.

In this paper, we treat the dense aluminum plasma consisting of N_e electrons, ion species such as N^+, N^{2+}, N^{3+}, and also N_a atoms, N_m molecules, N_m^+ molecular ions, occupied volume V at temperature T. The free energy of such system have a form:

$$\beta F = -\sum_k N_k ln\frac{eV\Sigma_k}{N_k\lambda_k^3} - \sum_k Z_k^2 N_k \Delta f(N_k) - \frac{N_i N_a}{V} B_{ia}(T), \qquad (1)$$

where $\beta = \frac{1}{k_B T}$ – inverse temperature, k_B – Boltzmann constant, $\lambda_k = \left(\frac{2\pi\hbar^2\beta}{m_k}\right)^{1/2}$ - thermal de-Broglie wavelength of a particle of species k, $k = e, A^+, A^{2+}, A^{3+}, A, A_2, A_2^+$; Δf – correction to free energy from charge-charge interaction, $B_{ia}(T)$ – ion-atom virial coefficient.

To take into account the interaction of free charges the Debye theory in grand canonical ensemble [5] was used.

We restricted the account of ion-atom interaction. This choice caused by the fact that the bond energy of ion in molecular ion is approximately equal $1.7\ eV$ [7], but electron affinity is in order of value $0.3 - 0.5\ eV$. Besides, the ground state of electron in negative ion is p-state, that mean impossibility of sequential description of electron-atom interaction using sphericalsymmetric potential and hence use of classical virial coefficients. The virial coefficient of the ion-atom interaction in a free state for the polarization potential have been calculated in [6].

Composition of aluminum plasma was calculated from equations of chemical equilibria using relations for the electroneutrality $N_e = N^+ + 2N^{2+} + 3N^{3+} + N_m^+$ and the total particle number $N = N_a + N^+ + N^{2+} + N^{3+} + 2(N_m + N_m^+)$.

The partition function of an atom have been calculated in Planck-Larkin approximation with use of statistical weights and binding energies for an atom of aluminum from database of National Institute of Standards and Technology: http://physics.nist.gov.

The partition functions of the molecule and molecular ion were defined in the following way:

$$\Sigma_{m,m^+} = exp(\beta D) exp(\beta \varepsilon_{m,m^+}) Z_{rot} Z_{vib}, \tag{2}$$

here D – atomization energy of a molecule (molecular ion) [7], Z_{rot}, Z_{vib} – the rotational and vibration partition functions accordingly, calculated in approximation of rigid rotator - harmonic oscillator with use of known data for calculation of moments of inertia [7] and vibration frequencies [8]. ε_{m,m^+} – constant defining the reference point of energy in reaction of dissociation of a molecule (molecular ion). So for reaction $m \to A + A$ it is equal $\varepsilon_m = 2I$ and for reaction $m^+ \to A + A^+$ $\varepsilon_{m^+} = I$. The choice of the reference point of energy is rather important for a derivation of expression for internal energy.

As a result, expressions for caloric and thermal EOS have been received:

$$\beta P = \frac{\partial \beta F}{\partial V} = \sum_k n_k - \frac{\widetilde{\Gamma}_D}{6} \sum_k \frac{Z_k^2 n_k}{1 + Z_k^2 \widetilde{\Gamma}_D / 2} - n_i n_a B_{ia}(T), \tag{3}$$

$$\begin{aligned} E &= \frac{\partial \beta F}{\partial \beta} = \frac{3}{2} k_B T \sum_k N_k - \frac{\widetilde{\Gamma}_D}{2} \sum_k \frac{Z_k^2}{1 + Z_k^2 \widetilde{\Gamma}_D / 2} - \Delta e_{ia} - \\ &- N_a < E_a > - N_m < E_m > - N_m^+ < E_m^+ > - N^+ < E^+ > - N^{2+} < E^{2+} >, \end{aligned} \tag{4}$$

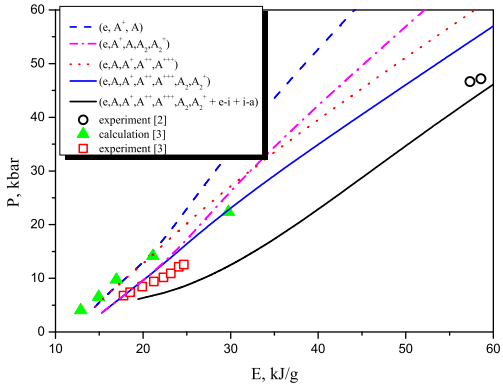

Figure 1: Pressure as a function of the specific internal energy along isochore $V/V_0 = 9$

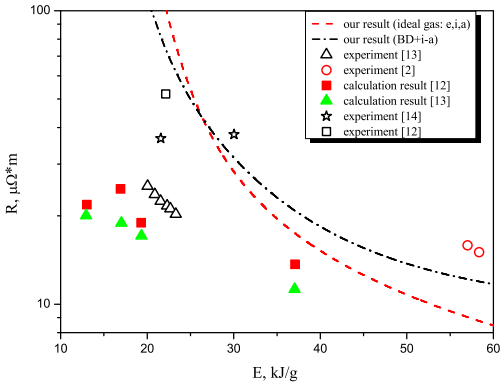

Figure 2: The electrical resistivity of aluminum vs the specific internal energy along isochore $V/V_0 = 9$

here $\Delta e_{ia} = \frac{3}{4} k_B T n_i N_a B_{ia}(T)$ – the correction to energy from the ion-atom interaction;

$< E_j >= \frac{1}{\Sigma_j} \frac{\partial \Sigma_j}{\partial \beta}$ – an average energy of a particle of species j ($j = m, m^+, A, A^+, A^{2+}$).

It is necessary to set a zero of the reference point of internal energy and it is enough arbitrary procedure: $\widetilde{E} = E - E_0$. The reference point of the energy in chemical model (1) was chosen from a requirement, that it tends to a zero when the temperature tend to zero. In that case energy $E_0 = N_m \langle E_m \rangle = N(D/2 + I)$. For comparison with concrete experiments, it is necessary to attached to the experimental origin of the energy - metal at ambient temperature: $E_{cal} = N(E_{mel} + E_{ev}) + \widetilde{E}$, where E_{mel} and E_{ev} – specific melting and evaporation energy.

Using expressions (3, 4) dependencies of pressure on internal energy of plasma are derived. The isochore $V/V_0 = 9$ in ideal-gas approximation for various component composition of plasma, and also data of experiments [1, 2] are presented in Fig. 1. It is shown, that account of molecules and molecular ions considerably affected on behavior of isochore in initial phase of heating. In a high-energy region the multiply charged ions played an important role. Coulomb interaction is considerable at high energies where plasma is practically fully ionized. Ion-atom interaction give a considerable correction on behavior of isochore at low temperatures (energies). Comparison of dependence of resistance of aluminum vapor plasma on internal energy with various experimental data [1, 9, 10, 11] is shown on Fig. 2. Interpolation Frost's formula was used to calculate electrical conductivity. Electron-ion transport cross-section was calculated using Rutherford formula. Transport cross-sections for electron-atom and electron-molecule scattering was calculated using Wigner formula for resonance scattering at low energies. It is shown, that at high energies there is good agreement with measured conductivity. It is necessary

to take into account formation of polyatomic clusters and to improve expressions for transport cross-sections of electron scatterer in dense metal vapor.

Conclusion. The chemical model of non-ideal gas-plasma mixture for the description of the dense aluminum vapor plasma consisting of electrons, various species of ions, atoms, molecules and molecular ions is suggested. Caloric and thermal equations of state and composition of plasma were received. The important role of molecules and molecular ions of aluminum, especially in an initial stage of the metal vapor heating is showed. The satisfactory agreement with experimental data [1, 2] in the region of applicability of model is received.

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