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A wide-range multiphase equation of state for Pt

V.M.Elkin, V.N.Mikhaylov, A.A.Ovechkin, N.A.Smirnov

V.N.Mikhaylov@vniitf.ru

The work presents a semi-empirical wide-range EOS for Pt considering melting, evaporation, and ionization, based on a wide spectrum of experimental and calculation data. In the regions where no experimental data were available, we used data from first-principles and average-atom model calculations. The EOS was used to calculate the melting curve of platinum to pressure above 1 TPa, sound speeds along the shock Hugoniot, parameters of melting under shock compression, and the critical point.

The free Helmholtz energy reads as

(1) $$F(V,T) = F_C(V) + F_A(V,T) + F_E(V,T) - S_{Tr}T,$$

where V is molar volume, $F_C=E_C$ is cold energy at $T=0K$, F_A и F_E are thermal contributions from atoms and thermally excited electrons, and $S_{Tr}T$-provides the experimental value for the entropy jump during melting.

The cold energy is written as follows

In the compression at x<1:

(2) $$E_C(V) = E_{0K} - \int_{V_{0K}}^{V} P_C(V)dV$$

$$P_C(y) = 3B_{0K}\frac{1-y}{y^5}\exp\left[C_0(1-y)\right]\left\{1 + C_1y(1-y) + C_2y(1-y)^2 + C_3y(1-y)^3\right\}$$

In the tensile range at x>1:

(3) $$E_C(x) = V_{0K}\left[\frac{A}{m}\left(x^{-m}-1\right) + \frac{B}{n}\left(x^{-n}-1\right) + \frac{C}{k}\left(x^{-k}-1\right)\right] + E_{0K}$$

$$P_C(x) = Ax^{-(1+m)} + Bx^{-(1+n)} + Cx^{-(1+k)}$$

where $x=V/V_{0K}$, $y=x^{1/3}$, V_{0K} and B_{0K} are molar volume and bulk modulus at $x=1$

The thermal component F_A (for solid phase) is written as

(4) $$F_A(V,T) = 3RTf(\tau) - A_{Ah}RT\left(e^{\tau}-1\right)^{-1}$$

$$f(\tau) = \frac{3}{8}\tau + \ln(1-e^{-\tau}) - \frac{1}{3}D(\tau), \quad \tau = \frac{\theta(V)}{T}, \quad D(\tau) = \frac{3}{\tau^3}\int_0^{\tau}\frac{x^3dx}{e^x-1}, \quad \theta(V) - \textit{Debye temperature}$$

The Gruneisen function is taken in the form of the empirical expression

(5) $$\Gamma(V) = \frac{2}{3} + \frac{\left(\Gamma_0 - \frac{2}{3}\right)\left(B_A^2 + D_A^2\right)}{B_A^2 + \left(D_A - \ln x\right)^2}$$

The Debye temperature is determined from the integration of $\Gamma(V) = -\frac{\partial \ln\theta(V)}{\partial \ln V}$

(6) $$\theta(V) = \theta_0\exp\left\{-\int_{V_{OK}}^{V}\frac{\Gamma(V)}{V}dV\right\} = \theta_0 x^{-\frac{2}{3}}\exp\left\{\frac{\left(\Gamma_0-\frac{2}{3}\right)\left(B_A^2+D_A^2\right)}{B_A^2}\left[arctg\frac{D_A-\ln x}{B_A} - arctg\frac{D_A}{B_A}\right]\right\}$$

In the liquid region the thermal component is written as

(7) $$F_A(V,T) = \frac{3RT}{2}\left[1 + \frac{x_a}{x+x_a}\cdot\frac{T_a}{T+T_a}\right]\ln\left[\frac{T_{as}\left(\theta_L(V) + Tx^{-2/3}\right)}{T\left(T+T_{ac}\right)}\right]$$

The electron component F_E is written as:

(8) $$F_E(V,T) = -C_E(V,T)T\ln\left[1 + \frac{B_E(T)T}{2C_{Ei}}x^{\Gamma_E(V,T)}\right]$$

$$B_E(T) = \frac{2}{T^2}\int_0^T\int_0^{\tau}\beta(t)dtd\tau, \qquad C_{Ei} = \frac{3RZ}{2},$$

$$C_E(V,T) = \frac{3R}{2}\left[Z + (1-Z)q_e\frac{x^{n_z}}{(x^{n_z}+x_Z^{n_z})}\frac{T_Z^{m_z}}{(T^{m_z}x^{s_e}+T_Z^{m_z})}\right]\exp\left(-\frac{\tau_i}{T}\right)$$

$$\tau_i = T_i\exp\left(-\frac{x}{x_i}\right)$$

$$\Gamma_E(V,T) = \Gamma_{Ei} + \left(\Gamma_{E0} - \Gamma_{Ei} + \gamma_m\frac{T}{T_g}\right)\exp\left(-\left(\frac{T}{T_g}\right)^{n_g} - \frac{x_d}{x}\left(\frac{x}{x_e}-1\right)^2\right)$$

$$\beta(T) = \beta_i + \left(\beta_0 - \beta_i\right)\exp\left(-\frac{T}{T_b}\right)$$

As $T \to \infty$ free energy (8) tends to the expression for the ideal gas of fully ionized electrons

Table 1. Phase transition in liquid of platinum on Hugoniot

	Pressure, GPa	Temperature, K
This work	464.7 – 634.3	1772 – 13718
Lomonosov EOS	400 – 570	9350 – 11566

Table 2. Critical point parameters for platinum

Temperature, K	Pressure, GPa	Density, g/ccm	Source
12526	1.05	5.419	Hard-sphere model [Young]
14330	0.87	5.02	Law of corresponding states [Fortov]
9285	0.949	4.72	Soft-sphere model [Savrasov]
9758	0.669	3.921	Soft-sphere model [Levashov]
11430	0.621	5.236	Lomonosov EOS
12129	0.67	4.77	This work

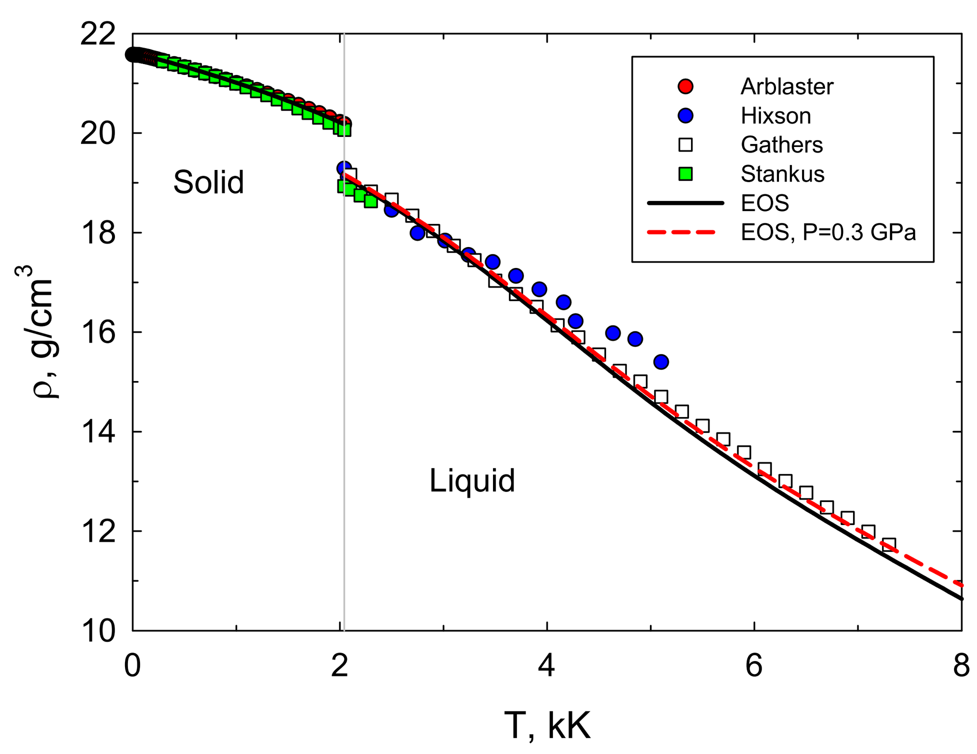

Fig. 1. Density versus temperature for solid and liquid platinum (dashed line for 0.3GPa).

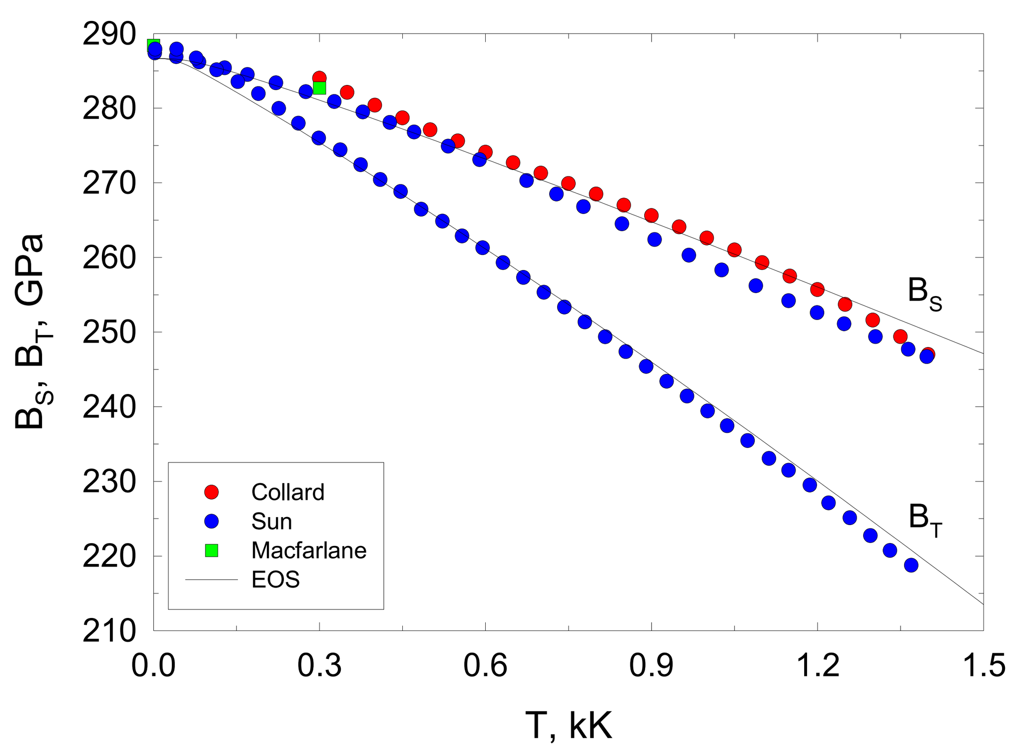

Fig. 2. Adiabatic and isothermal bulk moduli versus temperature

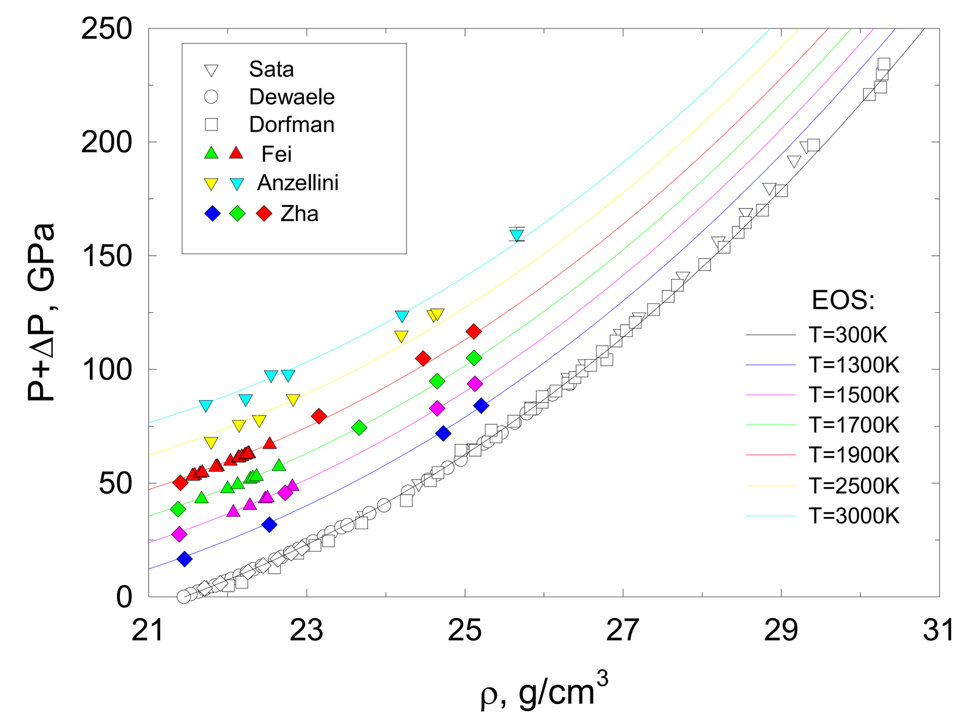

Fig. 3. Solid platinum compression isotherm

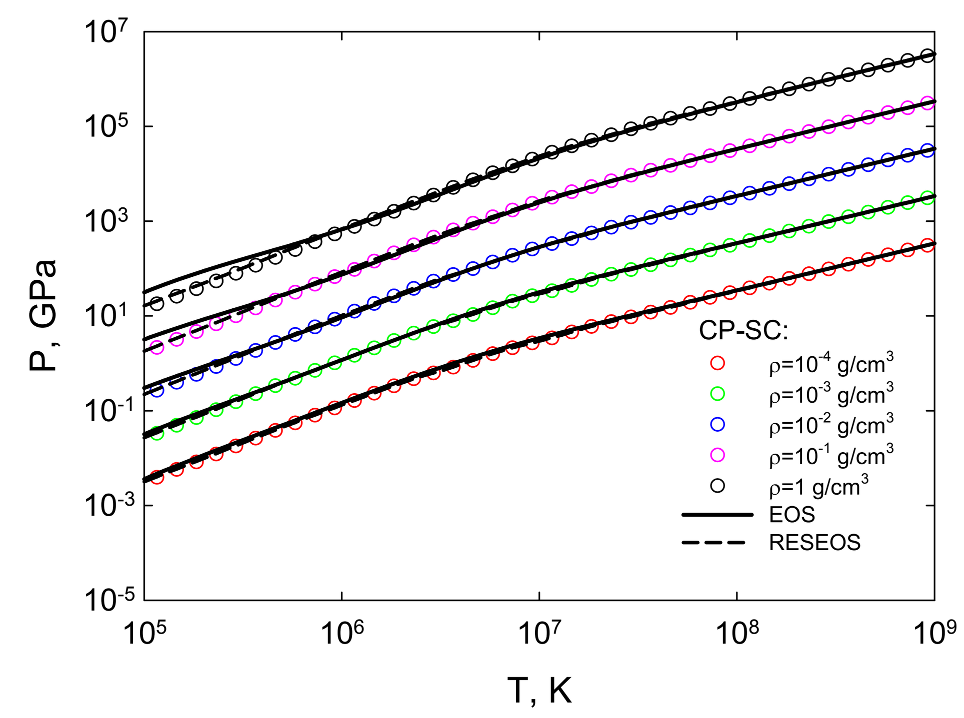

Fig. 4. Platinum isochores at low densities

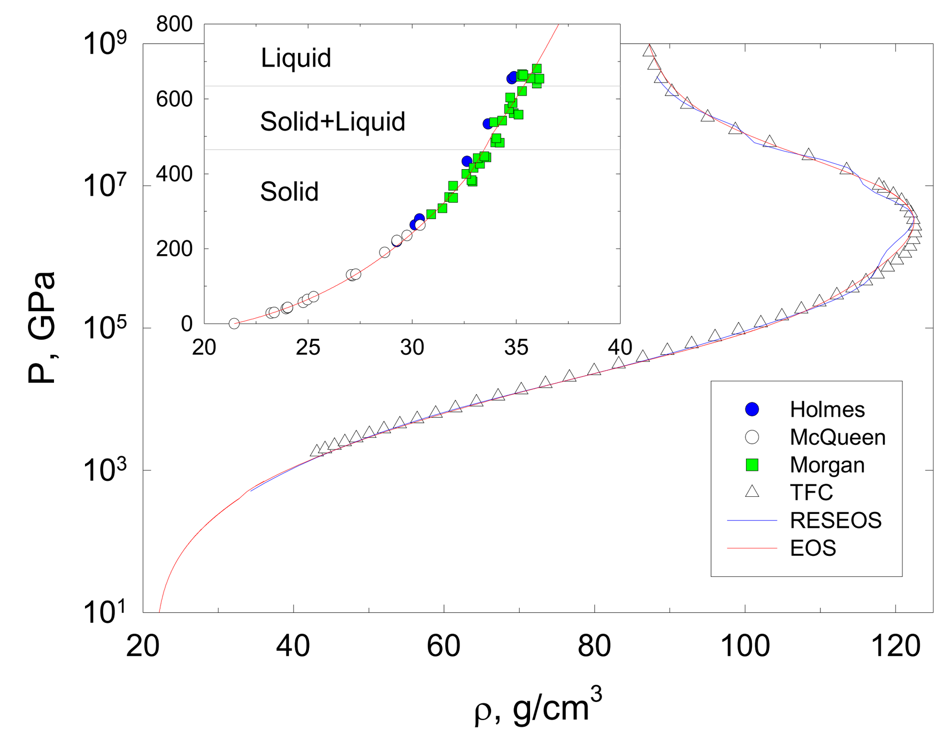

Fig. 5. Shock Hugoniot of platinum

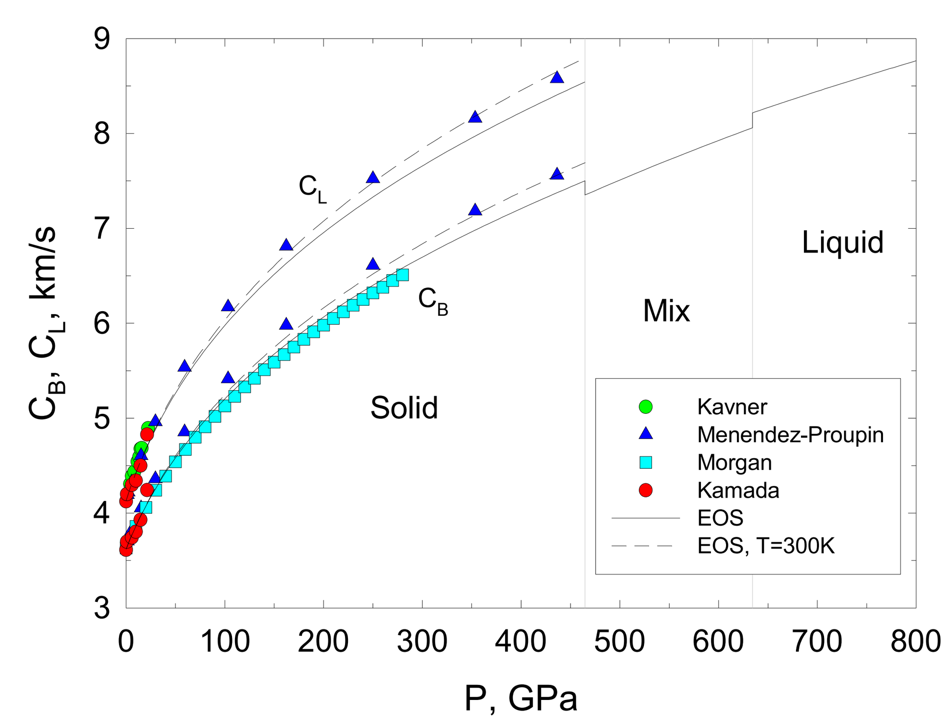

Fig. 6. Longitudinal and bulk sound velocities versus pressure on shock Hugoniot and on the isotherm 300K.

Phase diagram:

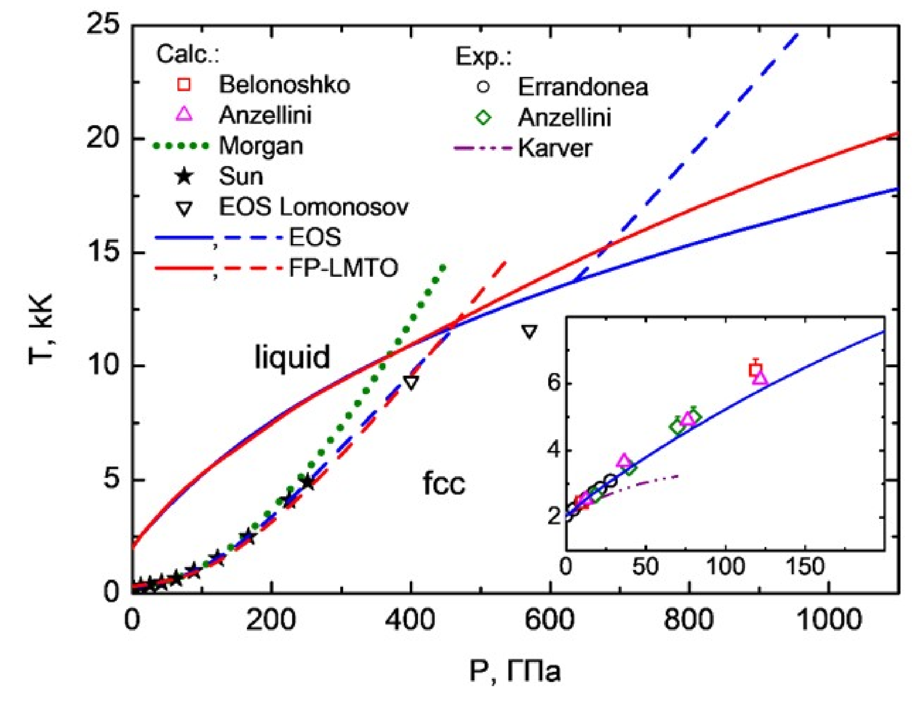

Fig. 7. Phase diagram for platinum

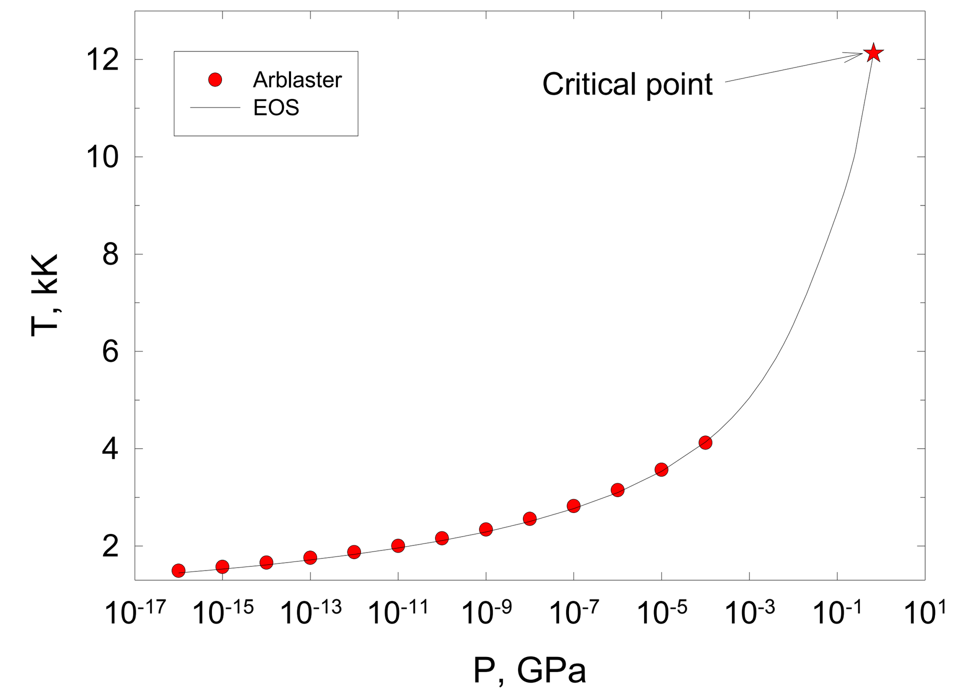

Fig. 8. Evaporation temperature versus pressure with the critical point