THE EQUATION OF STATE OF IRON UP TO PRESSURES OF SEVERAL MILLION ATMOSPHERES

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Abstract

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V. N. Zharkov and V. A. Kalinin

THE EQUATION OF STATE OF IRON UP TO PRESSURES OF SEVERAL MILLION ATMOSPHERES

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Below a new method is proposed for determining the equation of state of metals at high pressures with the aid of the experimental Hugoniot adiabat ([1–6]). Specifically, the equation of state of iron has been obtained.

The Hugoniot adiabat for iron is shown in Fig. 1. It was constructed from the experimental data of Bancroft et al. ([1]), who discovered a polymorphic transition at $p \simeq 1.31 \cdot 10^5$ atm. (experimental data up to $2 \cdot 10^5$ atm.); from the data of Walsh et al. ([2]) (experimental data up to $4.8 \cdot 10^5$ atm.) and from the data of Al' tshuler et al. ([4]) (experimental data for pressures $> 5 \cdot 10^5$ atm.). The break in the iron adiabat at the point $1.31 \cdot 10^5$ atm. leads to the fact that above this point the shock wave is unstable and splits into two ([1,2]): one connecting the point $p_0 = 0$ atm., $x_0 = 1$ with the point $p_1 = 1.3 \cdot 10^5$ atm., $x_1 = 0.9356$, and another beginning at the point $p_1 = 1.31 \cdot 10^5$ atm. ($x = V/V_0$ is the relative volume, V_0 is the volume under normal conditions). Beginning with pressures $p_\Gamma \geq 3.5 \cdot 10^5$ atm., the shock wave again becomes stable, and the equation of the shock adiabat has the form

$$E_\Gamma = E_0 + \frac{1}{2\rho_0} p_\Gamma (1 - x), \qquad \rho_0 = 7.84 \ \frac{\text{g}}{\text{cm}^3}, \tag{1}$$

$E_0 = -3.6454 \cdot 10^{11}$ erg/g (the energy of α-Fe under normal conditions ([7]), see below). At sufficiently low temperatures the contribution of thermally excited conduction electrons to the pressure and energy may be neglected (this corresponds to the initial segment of the adiabat up to pressures $p_\Gamma \lesssim 10^6$ atm.). Under these conditions the energy and pressure may be represented as the sum of the potential parts $E(x)$ and $p(x)$ and the thermal parts $E_T(x, T)$ and $p_T(x, T)$ (caused by phonons). For the potential parts $E(x)$ and $p(x)$ we adopt the semiempirical equations proposed by B. I. Davydov ([7]) for metals, and for $E_T(x, T)$ and $p_T(x, T)$ the usual Debye expressions. Then

$$E = \Phi(x) + \frac{9}{8}\frac{R\theta}{\mu} + \frac{3RT}{\mu} D\left(\frac{\theta}{T}\right), \qquad \Phi(x) = \frac{3}{\rho_0}\left(b^{-1}\Sigma - k_2 x^{-1/3}\right); \tag{2}$$

$$P = P_0(x) + \frac{\rho_0\gamma}{x}\left[\frac{9}{8}\frac{R\theta}{\mu} + \frac{3RT}{\mu}D\left(\frac{\theta}{T}\right)\right], \qquad P_0(x) = \Sigma x^{-2/3} - k_2 x^{-4/3}, \quad (3)$$

where

$$\Sigma = k_1 e^{-bx^{1/3}} \equiv Ae^{b(1-x^{1/3})}, \qquad D(z) = \frac{3}{z^3}\int_0^z \frac{y^3\,dy}{e^y - 1};$$

k_1, k_2, b are constants to be determined from experimental data; $\theta = \theta(x)$ is the Debye temperature; $\mu = 56$ (for iron) is the molecular weight; R is the gas constant; γ is the Grüneisen parameter; T is the temperature in °K. For the Grüneisen parameter we use the Dugdale-MacDonald formula ([8,2]), and since γ, by definition, depends only on volume, we compute

it by means of the zero isotherm $P_0(x)$; then

$$\gamma(x) = -\frac{1}{3} - \frac{x}{2}\frac{d^2(Px^{2/3})/dx^2}{d(Px^{2/3})/dx} = \frac{1}{6}\frac{\sum(bx^{1/3})^2 - 6b_2x^{-2/3}}{\sum(bx^{1/3}) - 2k_2x^{-2/3}}. \qquad (4)$$

For α-Fe the constants in equations (2) and (3) were determined by B. I. Davydov[7] from Bridgman' s data: $k_1 = 7.8722 \cdot 10^8$ bar, $k_2 = 1.1522 \cdot 10^6$ bar (1 bar $= 10^6$ dyn/cm^2); $b = 6.5345$; the Debye temperature of iron under normal conditions is known and is equal to $\theta_0 = 420^\circ$ K. The quantity E_0 in (1), expressed in terms of the parameters of the first phase by means of (2), has the form

$$E_0 = \Phi(1) + \frac{9}{8}\frac{R\theta_1}{\mu} + \frac{3RT_0}{\mu}D\left(\frac{\theta_1}{T_0}\right). \qquad (5)$$

Our problem is to determine the constants A, b, k_2 for the high-pressure phase. First of all it should be taken into account that the energy of the second phase $\Phi''(x)$ must be correctly normalized with respect to the energy of the first phase $\Phi'(x)$ (in (1), E_0 enters (5)). This is easy to do if one observes that the difference of the energies on the zero isotherms of the second and first phases at a certain fixed pressure P, and under the assumption of equality of the Debye temperatures $\theta'' = \theta'$ (two primes denote the high-pressure phase, one prime the low-pressure phase), is equal to

$$\frac{P}{\rho_0}[x'(P) - x''(P)].$$

Let $x' = x_1$ be the transition point, the corresponding point of the high-pressure phase $x'' = y$. The point y is readily determined by the intersection of the zero isotherm of the high-pressure phase with the straight line $p_0'(x_1)$ on the (p, x)

Figure 1

Figure 1: Figure 1

diagram. As a result, of the three parameters $A'', k_2'',$ and b'' to be determined, we can express k_2'' in terms of $A'', b'', y,$ and the known characteristics of the first phase:

Fig. 1. 1 –Hugoniot shock adiabat; 2 –zero isotherm of iron after the transition; 3 –zero isotherm of iron before the transition[7]; 4 –temperature T on the shock adiabat; 5 –temperature of melting T_0, divided by 2.

$$k_2'' = y^{1/3}(b'')^{-1}A''e^{b''(1-y^{1/3})} - \frac{\rho_0}{3}\,y^{1/3}\left[\Phi'(x_1) + \frac{p_1}{\rho_0}(x_1 - y)\right]. \qquad (6)$$

In doing this we assumed that $\theta''(y) = \theta'(x_1) = 420^\circ$ K. The remaining two parameters A'' and b'' were determined by the method of least squares using the experimental Hugoniot adiabat (see Fig. 1) and the theoretical formula for this adiabat

$$p_\Gamma = \left\{p_0''(x) + \frac{\rho_0\gamma''}{x}\left[E_0 - \Phi''(x)\right]\right\}\left\{1 - \frac{\gamma''(1-x)}{2x}\right\}^{-1}. \qquad (7)$$

The latter is obtained by eliminating the temperature from equations (1), (2), and (3). The experimental points that were used are given in Table 1. To determine $A'', k_2'',$ and b'', experimental points up to $x = 0.7273$ were used; in this case the experimental pres–

···at this point $p_\Gamma = 1.065 \cdot 10^6$ bar was reduced to $p_\Gamma = 1.04 \cdot 10^6$, since preliminary estimates gave for p_{el} at this point a value $\sim 3 \cdot 10^4$ bar. The values of the parameters A'', k_2'', and l'' turned out to be $A'' = 9.4389 \cdot 10^5$ bar, $k_2'' = 1.0740 \cdot 10^6$ bar, $l'' = 7.7845$. The theoretical pressures on the Hugoniot adiabat (7) calculated with these parameters are also given in Table 1. At high temperatures and pressures (which corresponds to the upper portion of the shock adiabat, $P_\Gamma > 10^6$ atm.) one must take into account the contribution to the energy and pressure of the metal from thermally excited conduction electrons. At pressures $\sim 5 \cdot 10^6$ atm. and temperatures $\sim 10^{4\circ}$K the shell structure of the atoms is still well preserved, and consequently the contribution of the potential and lattice parts to the energy and pressure is still given by equations (2) and (3). The contribution of thermally excited conduction electrons to the energy E_{el} has the standard form ([8])

$$E_{\text{el}} = \frac{1}{2}\delta x^{2/3}\alpha T^2, \qquad \delta = \left(\frac{\pi}{3}\right)^{2/3}\frac{k^2 m N_0^{1/3}}{\mu\hbar^2}\left(\frac{\mu}{\rho_0}\right)^{2/3}, \qquad \alpha = z^{1/3}\frac{m^*}{m}, \quad (8)$$

where k is Boltzmann' s constant; $\hbar$ is Planck' s constant divided by 2π; m is the mass of a free electron; m^* is the effective mass of a conduction electron; N_0 is Avogadro' s number; z is the number of conduction electrons per atom. In (8) δ is a constant, and we shall regard the quantity α as a function of volume, $\alpha = \alpha(x)$. Then the contribution of thermally excited conduction electrons to the pressure p_{el} is

$$p_{\text{el}} = \frac{1}{2}\delta\rho_0 x^{-1/3}\alpha g T^2, \qquad g = \frac{2}{3} + \frac{d\ln\alpha}{d\ln x} = \frac{x}{\rho_0}\frac{p_{\text{el}}}{E_{\text{el}}}, \tag{9}$$

where g is the "electronic" analogue of the Grüneisen parameter. For transition metals of the iron type $\alpha > 10$, while the behavior of the quantity g has not been studied at all. Let us choose the dependence of α on volume in the form

$$\alpha = \alpha_0 e^{B(x^{1/3}-1)}, \qquad g = \frac{2}{3} + \frac{B}{3}x^{1/3}, \tag{10}$$

where the constants α_0 and B will be determined with the aid of the upper branch of the experimental Hugoniot adiabat. To determine α_0 and B, three upper experimental points ([4]) on the shock adiabat were used (see Table 1). The temperature on the shock adiabat can be determined both from the equation for the energy (2) + (8), and from the equation for the pressure (3) + (9). The quantities α_0 and B were chosen so that both determinations of the temperature led to coincident results. It turned out that $\alpha_0 = 17.2$, $B = 9.86$. The temperatures determined both from the energy equation and from the pressure equation for the three upper experimental points differ by approximately 2%. This indicates that the choice of the dependence of α on volume (10) was successful.

Table 1

	x	x	x	x	x	x	x	x	x	x
	0.8710	0.8315	0.8289	0.8181	0.8149	0.8080	0.7273	0.6684	0.601	0.5960
$p_\Gamma \cdot 10^{-5}$, exper., bar	2.00	3.584	3.667	4.249	4.347	4.808	(10.40)	18.5	35.6	40.2
$p_\Gamma \cdot 10^{-5}$, theor. (7), bar	1.975	3.59	3.71	4.23	4.38	4.74	10.4	–	–	–

	x	x	x	x	x	x	x	x	x	x
$p_\Gamma \cdot 10^{-5}$, theor. (11), bar	–	–	–	–	–	4.79	10.7	18.27	36.27	38.55

Eliminating the temperature from the equations for the energy and pressure of the metal on the shock adiabat, we obtain a theoretical formula for the Hugoniot adiabat of iron, analogous to formula (7), with allowance for the electronic terms,

$$p_\Gamma = \frac{n_2 - \sqrt{n_2^2 - 4n_1 n_3}}{2n_1}, \tag{11}$$

where

$$n_1 = \frac{1}{\rho_0^2}\left[\frac{x}{g} - \frac{1}{2}(1-x)\right]^2;$$

$$n_2 = \frac{1}{\rho_0}\left\{\frac{2\gamma(3R/\mu)^2(1-\gamma/g)}{\delta x^{2/3}\alpha g}\left[\frac{x}{\gamma} - \frac{1}{2}(1-x)\right] + \right.$$

$$\left. +2\left[\frac{x}{g} - \frac{1}{2}(1-x)\right]\left[\frac{x}{\rho_0 g}p_0(x) + E_0 - \Phi(x)\right]\right\};$$

$$n_3 = \left\{\frac{2\gamma(3R/\mu)^2(1-\gamma/g)}{\delta x^{2/3}\alpha g}\left[\frac{x}{\rho_0\gamma}p_0(x) + E_0 - \Phi(x)\right] + \right.$$

$$\left. + \left[\frac{x}{\rho_0 g}p_0(x) + E_0 - \Phi(x)\right]^2\right\}.$$

The temperature on the shock adiabat (11) is determined by the formula

$$T = \{E_\Gamma - \Phi(x) - (x/\rho_0 g)[p_\Gamma - p_0(x)]\}\{(3R/\mu)(1-\gamma/g)\}^{-1}. \tag{12}$$

Figure 1 gives the theoretical shock adiabat (11) for points $x \leqslant 0.8315$, and the temperature on it (12), and also plots the degeneracy temperature of the conduction electrons T_0, divided by z: $T_0/z = \pi^2 R/2\mu\delta\alpha x^{2/3}$. The theoretical adiabat (11) can be extrapolated to the region $p_\Gamma \sim 10^7$ bar ($x \sim 0.55$). At $x \sim 0.55$ the quantity $n_2^2 - 4n_1 n_3$ in (11) changes sign and becomes negative. This is connected with the fact that the temperatures on the shock adiabat in

this region, $\sim 3.0 \cdot 10^4$ °K, become close to the degeneracy temperature T_0/z, and, consequently, the use of expressions (8) and (9) becomes illegitimate. The latter is manifested in the incompatibility of the basic equations in this region.

Ya. B. Zel' dovich [6] proposed using two shock adiabats for the same metal in determining the equation of state, choosing specimens in the porous and solid states.

In the case of a porous specimen,

$$E_\Gamma = E_0 + \frac{p_\Gamma}{2\rho_0}(x_{0\,\mathrm{por}} - x), \qquad x_{0\,\mathrm{por}} = \frac{\rho_0}{\rho_{0\,\mathrm{por}}}.$$

Equation (11) is retained; it is only necessary to replace, in n_1 and n_2, the bracket $(1-x)$ by $(x_{0\,\mathrm{por}} - x)$. The experimental data [3] for porous specimens with $\rho_{0\,\mathrm{por}} \sim 5.5$ g/cm^3 and $p_\Gamma > 10^6$ atm lead to excessively high T_Γ, where the formulas obtained in this work are inapplicable. Knowledge of two shock adiabats would make it possible to determine independently the electronic parameters α and g as functions of the volume x. In this connection a shock adiabat with $\rho_{0\,\mathrm{por}} \gtrsim 7$ g/cm^3 would be of interest. We also note that the zero isotherm obtained by us for the high-pressure phase (Fig. 1) is close to that determined by L. V. Al' tshuler et al. [3], and is located above the latter by $\sim 10^5$ atm.

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Institute of Physics of the Earth named after O. Yu. Schmidt
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Note: Figure translations are in progress. See original paper for figures.