Equations of State of Al, Au, Cu, Pt, Ta, and W and Revised Ruby Pressure Scale[1]

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Recently [1–4], the ruby pressure scale, in which pressure is measured on the basis of the R_1 line shift of ruby luminescence, has been reconsidered. The well-known ruby scale of Mao et al. [5], which was calibrated using room-temperature isotherms of Cu and Ag reduced from shock-wave data of Carter et al. [6], has been significantly shifted towards the ruby pressure scale of Aleksandrov et al. [7], based on an a priori equation of state of diamond. Various functional dependences of pressure on the R_1 line shift of ruby luminescence have been proposed. The best known and most popular scale [5] looks as follows:

$$P = \frac{A}{B}\left[\left(1 + \frac{\Delta\lambda}{\lambda_0}\right)^B - 1\right], \qquad (1)$$

where $A = \lambda(dP/d\lambda) = 1904$ GPa, $B = 7.665$, $\lambda_0 = 694.24$ nm (Fig. 1).

Aleksandrov et al. [7] have proposed a ruby pressure scale in the form

$$P = A\left(\frac{\Delta\lambda}{\lambda_0}\right)\left(1 + \frac{m\Delta\lambda}{\lambda_0}\right), \qquad (2)$$

where $A = 1892 \pm 13$ GPa and $m = 6.4$, which differs considerably from expression (1).

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The three-parameter ruby pressure scale of Holzapfel [1] has the following form:

$$P = \frac{A}{B+C}\left[\exp\left(\frac{B+C}{C}\left(1 - \left(\frac{\lambda}{\lambda_0}\right)^{-C}\right)\right) - 1\right], \qquad (3)$$

where $A = 1820$ GPa, $B = 14$, $C = 7.3$, which also differs from expression (1).

Kunc et al. [3, 4] insist that the scale (2) should be written in the form

$$P = A\left(\frac{\Delta\lambda}{\lambda}\right)\left(1 + \frac{\mu\Delta\lambda}{\lambda}\right), \qquad (4)$$

where $A = 1860$ GPa and $\mu = 7.75$. Kunc et al. [3, 4] note that scale (4) with parameters $A = 1820$ GPa and $\mu = 7.9$ practically coincides with scale (3) up to 200 GPa.

Though different methodological approaches have been used for the calibration of the ruby pressure scale in [1–4], very similar results have been obtained. Dorogokupets and Oganov [2] have constructed the equations of state of Cu and Ag for a wide range of temper-
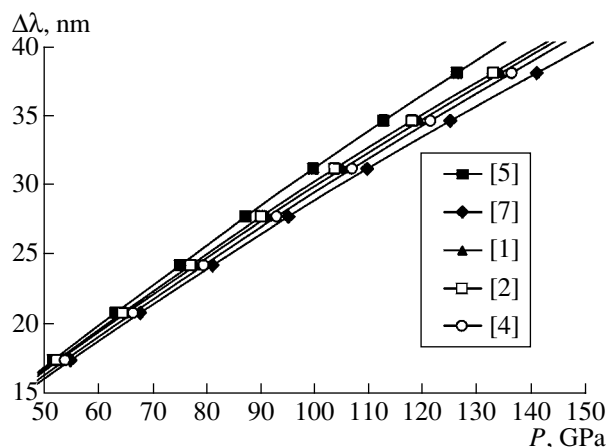

Fig. 1. Different calibrations of the ruby pressure scale. The scale of [2] has the form (1) with parameters $A = 1871$ GPa and $B = 10.06$.
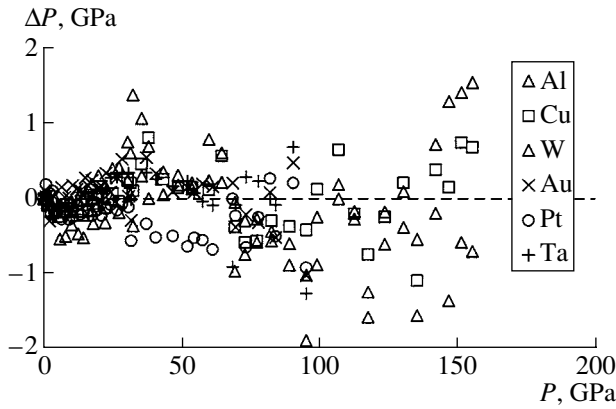
Fig. 2. Comparison of the data of Dewaele et al. [8], calibrated using our ruby pressure scale (12), with room-temperature isotherms of Al, Au, Cu, Pt, Ta, and W given in the table.

Fig. 3. Difference between published ruby pressure scales extrapolated to 300 GPa plotted as a function of the R_1 line shift of ruby luminescence. ΔP is the difference between our scale and others. The scale of reference [12] is shown in two variants (see text). Dashed lines correspond to a difference of 2%.

atures and pressures, agreeing with thermochemical, X-ray, and ultrasonic data and with the recent approximation of the shock-wave data of N.N. Kalitkin and L.V. Kuz'mina for Cu (U_S = 3.923 + 1.511U_p), Dokl. Phys. **47**, 778 (2002). Comparison of the calculated room-temperature isotherms of Cu and Ag with room-temperature isotherms from [6] has shown a difference of up to 2 GPa at a pressure of 70 GPa, which has resulted in a correction to the ruby scale [5]. In works [1, 3, 4], it has been shown that modern X-ray, phonon, and theoretical data for diamond on the room-temperature isotherm do not agree with the scale [5], which has also led to new ruby pressure scales in the form of Eqs. (3) and (4).

For calibration of the ruby pressure scale, it is necessary to recognize as revolutionary the work of Dewaele et al. [8], where *PV* relations at room temperature have been measured for Ta, Au, Pt, Al, Cu, and W up to 150 GPa in diamond anvil cells with a helium pressure-transmitting medium. When Dewaele et al. [8] compared the equations of state of these metals based on the ruby scale of Mao et al. [5] and the room-temperature isotherms obtained by reducing shock-wave data, it appeared that they differ by up to 10–12 GPa at pressures of 100–150 GPa. As a result, by correcting the ruby pressure scale for these differences, Dewaele et al. [8] have obtained a ruby pressure scale with parameters of *A* = 1904 GPa and *B* = 9.5 for Eq. (1). This scale gives practically the same pressures as the scales of Dorogokupets and Oganov [2] (see Fig. 3). Helium pressure-transmitting medium is believed to produce very nearly to hydrostatic conditions, which allows one to avoid stress in the diamond anvil cell; therefore, the Dewaele et al. data in [8] can be considered close to hydrostatic equilibrium. Using these measurements in combination with thermochemical, ultrasonic, X-ray, and shock-wave data enabled us to construct the equations of state of these metals and once again to refine the ruby pressure scale for quasi-hydrostatic conditions.
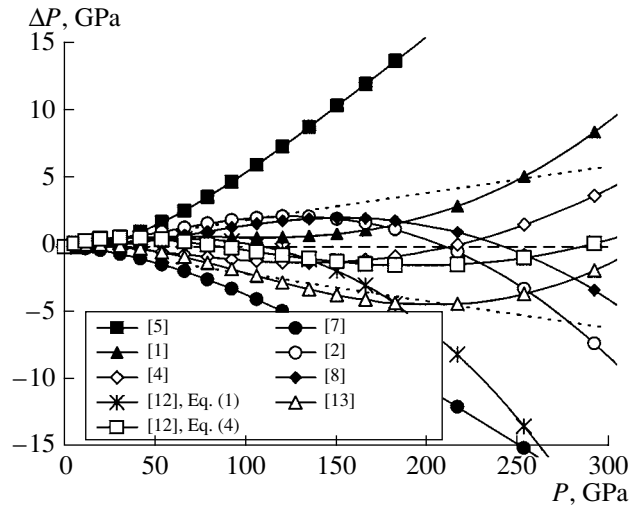
Let us write the Helmholtz free energy $F(V, T)$ as the sum [2, 9]:

$$F = U_0 + E(V) + F_{qh}(V, T) + F_{anh}(V, T)$$
$$+ F_{el}(V, T) + F_{def}(V, T), \qquad (5)$$

where U_0 is the reference energy; $E(V)$ is the potential (cold) part of the free energy on the reference isotherm, which depends only on volume; $F_{qh}(V, T)$, $F_{anh}(V, T)$, $F_{el}(V, T)$, and $F_{def}(V, T)$ are the quasi-harmonic part of the Helmholtz free energy; and the terms describing intrinsic anharmonicity, electronic contribution, and thermal defects, respectively, which depend on both volume and temperature.

Cold energy and pressure are determined from the Vinet equation of state written as (Vinet et al., J. Geophys. Res. **92**, 9319 (1987)):

$$P(V) = -\frac{\partial E}{\partial V} = 3K_0 y^{-2}(1 - y)\exp[(1 - y)\eta], \quad (6)$$

where $y = x^{1/3}$, $x = V/V_0$, $\eta = 1.5(K' - 1)$, and V_0 is molar volume at reference conditions (T_0 = 298.15 K, P_0 = 1 bar).

The quasi-harmonic part of the Helmholtz free energy is written as:

$$F_{qh} = \sum_1^i m_{Bi} R\left[\frac{d_i - 1}{2d_i}\theta_{Bi} - T\ln(1 + b_i)\right]$$
$$+ \sum_1^j m_{Ej} R\left[\frac{\theta_{Ej}}{2} + T\ln\left(1 - \exp\frac{-\theta_{Ej}}{T}\right)\right], \qquad (7)$$

where R is the gas constant, m_{Bi} and m_{Ej} are the numbers of degrees of freedom, and their sum should be equal to $3n$, where n is equal to number of atoms in the chemical formula; $b = [\exp(g) - 1]^{-1}$, $g = d\ln[1 + \theta_B/(Td)]$; d is the exponential parameter controlling the behavior of the low-temperature limiting behavior of the heat capacity; and θ_{Bi} and θ_{Ej} are the Bose–Einstein and the Einstein characteristic temperatures, which depend on volume written in the dimensionless form, $x = V/V_0$.

For the volume dependence of the Grüneisen parameter, we used the following form proposed by Al'tshuler et al. (J. Appl. Mech. Tech. Phys. **28**, 129 (1987) (see reference in [9])):

$$\theta = \theta_0 x^{-\gamma_\infty} \exp[(\gamma_0 - \gamma_\infty)(1 - x^\beta)/\beta], \qquad (8)$$

where γ_0 is the Grüneisen parameter under ambient conditions, γ_∞ is the Grüneisen parameter at $x = 0$, and β is a fitted parameter.

The intrinsic anharmonicity contribution to the Helmholtz free energy is taken according to the formulation of Oganov and Dorogokupets [10]:

$$F_{\text{anh}} = 3nR\frac{ax^m}{6}\left[\left(\frac{1}{2}\theta + \frac{\theta}{e^{\theta/T} - 1}\right)^2\right.$$

$$\left. + 2\left(\frac{\theta}{T}\right)^2 \frac{e^{\theta/T}}{(e^{\theta/T} - 1)^2}T^2\right]. \qquad (9)$$

The electronic component of the Helmholtz free energy is taken as

$$F_{\text{el}} = -\frac{3}{2}nRex^g T^2, \qquad (10)$$

where we assume the free-electron value $g = 2/3$ for Cu and Au (Zharkov and Kalinin in [2]).

For the contribution of thermal defects, which can be important at high temperatures, we use

$$F_{\text{def}} = -\frac{3}{2}nRT\exp\left(Sx^f - \frac{Hx^h}{T}\right), \qquad (11)$$

where S, H, f, and h are fitted parameters, but the latter two parameters were fixed for all metals: $f = -1$, $h = -2$.

Pressure on the shock-wave adiabat is calculated using the following equation:

$$P_H = \frac{P(V) - \frac{\gamma}{V}[E(V) - E_0]}{1 - \frac{\gamma(1 - x)}{2x}}.$$

Differentiating Eq. (5) with the account of Eqs. (6) and –(7) with respect to temperature at constant volume and with respect to volume at constant temperature, we obtain all necessary thermodynamic functions. With the above formulation, we can carry out a simultaneous processing of all the available measurements of the heat capacity, thermal expansion coefficient, volume, and adiabatic and isothermal bulk moduli at zero pressure, static measurements of volume on the room-temperature isotherm and at higher temperatures, and shock-wave data. We can also calculate any thermodynamic functions versus T and P (or versus T and V). It is necessary to note that, in the practical realization of the equations of state of metals, the Helmholtz free energy has been written as

$$F = U_0 + E(V) + F(V, T) - F(V, T_0).$$

Therefore, the obtained fitted parameters of equations of state of metals correspond to reference conditions $T_0 = 298.15$ K and $P_0 = 1$ bar. In addition, one should not forget that Eqs. (5)–(11) are written in terms of temperature and volume; therefore, for calculation of thermodynamic functions at given T and P, it is necessary first to find first the corresponding volume.

We have constructed semiempirical equations of state of Al, Au, Cu, Pt, Ta, and W for temperatures from 10–15 K up to melting temperature and compression up to $x = V/V_0 = 0.5$–0.6 using published experimental measurements of the heat capacity, thermal expansion coefficient, adiabatic bulk modulus at zero pressure, and shock-wave data from [11] (the resulting fitted parameters are shown in the table). Comparing the calculated room-temperature isotherms of these metals with the data of Dewaele et al. [8] and determining pressure with the ruby scale (1), we have obtained a difference of up to 12 GPa at the pressure of 150 GPa. To eliminate this difference, we recalibrated the ruby scale (1) and have obtained the following parameters: $A = 1885$ GPa and $B = 11$. However, the ruby pressure scale with these parameters holds only up to 100 GPa (see [9]). Therefore, we used the more flexible form (2) proposed by Aleksandrov et al. [7], and have obtained a new ruby pressure scale:

$$P = 1884\frac{\Delta\lambda}{\lambda_0}\left(1 + \frac{5.5\Delta\lambda}{\lambda_0}\right). \qquad (12)$$

Now, using the scale (12) instead of the scale (1) for calibration of pressure in Dewaele et al. [8] measurements, we obtain very good agreement with the room-temperature isotherms of Al, Au, Cu, Pt, Ta, and W; our isotherms can be calculated using parameters given in the table (Fig. 2). The maximum difference does not exceed 2 GPa up to a pressure of 160 GPa.

The obtained equations of state of Al, Au, Cu, Pt, Ta, and W are consistent with one another and with the new ruby pressure scale not only on the room-temperature isotherm. They also quite correctly describe the experimental measurements of heat capacity, thermal expansion coefficient, and adiabatic bulk modulus in a wide range of temperatures at zero pressure. One expects that the obtained equations of state will be correct at higher temperatures and pressures. The self-consistency of our equations of state can be checked not only on room-temperature isotherms, but also at higher temperatures

Fitted parameters of equations of state of metals

Parameter	Al	Au	Cu	Pt	Ta	W
V_0, cm^3	9.999	10.215	7.113	9.091	10.851	9.545
K_0, GPa	72.67	166.70	133.41	276.07	191.39	306.00
dK/dP	4.62	6.15	5.37	5.30	3.81	4.17
θ_{B1}, K	245.8	95.7	123.7	95.2	72.6	182.8
d_{B1}	5.575	8.290	3.776	8.199	5.536	13.270
m_{B1}	0.987	0.681	0.115	0.329	0.117	0.513
θ_{B2}, K	–	106.4	175.4	148.4	101.8	172.5
d_{B2}	–	3.239	10.372	4.005	24.513	3.305
m_{B2}	–	0.417	0.711	0.383	0.396	0.174
θ_{E1}, K	240.2	170.6	187.4	214.6	144.0	287.6
m_{E1}	1.000	1.063	0.756	1.211	1.118	1.166
θ_{E2}, K	356.2	105.2	286.9	140.8	214.9	213.8
m_{E2}	1.013	0.839	1.418	1.077	1.369	1.145
γ_0	2.144	2.960	1.974	2.802	1.714	1.553
γ_∞	1.017	0.978	1.554	1.538	1.241	0.694
β	3.942	2.590	4.647	5.550	6.825	3.698
a, K$^{-1} \cdot 10^6$	5.14	22.34	3.50	160.9	61.9	−39.3
m	3.439	3.450	3.465	4.060	4.000	2.671
e, K$^{-1} \cdot 10^6$	54.1	15.20	27.698	260.0	167.0	40.4
g^*	1.8	0.66	0.66	2.4	1.3	0.2
H, K	8679	11690	11690	32572	36278	14714
S	0.998	1.067	1.407	0.631	4.910	0.672

* V.N. Zharkov and V.A. Kalinin (see reference in [2]).

and pressures on the example of the simultaneous *PVT* measurements of the unit cell parameters of MgO, Pt, Ag, and Au (see [9]). All this allows us to recommend the equations of states of metals for pressure calibration at higher temperatures. Tables with the obtained *PVT* relations for these metals, and also for Ag and MgO, can be obtained from the authors.

Now, let us compare modern ruby pressure scales (Fig. 3). In [2], we used Mao et al. [5] measurements of the R_1 line shift of ruby luminescence and the unit cell parameters of Cu and Ag in the argon pressure-transmitting medium reported in [5]. Thermochemical, X-ray, ultrasonic, and shock-wave Cu and Ag data approximated by Kalitkin and Kuz'mina have been described using a general thermodynamic model similar to the one used here. As a result, the ruby pressure scale in the form (1) with parameters $A = 1871$ GPa and $B = 10.06$ (which passes between the scales of [5] and [7]) has been recommended.

Dewaele et al. [8] have carried out simultaneous measurements of unit cell parameters of six metals in helium pressure-transmitting medium and measurements of the R_1 line shift of ruby luminescence, which are the most accurate presently available data. Their calibration of the ruby pressure scale was based on the room-temperature isotherms of metals reduced from shock-wave data in the works of Wang et al. (2002), Hixson and Fritz (1992), and Nellis et al. (1988) (see references in [8]) and has led to a scale practically identical to our calibration of 2003 [2].

Chijioke et al. [12] also used the shock-wave data for the calculation of room-temperature isotherms of Al, Au, Cu, Pt, Ta, and W. They used ultrasonic measurements of bulk moduli at low pressure and considered the effects of stress on the shock-wave data. To calibrate the ruby pressure scale, Chijioke et al. [12] used the results of Dewaele et al. [8] and their own measurements of the unit cell parameters of gold depending on pressure. The ruby pressure scale obtained in [12] is given by Eqs. (1) and (4) with parameters $A = 1873 \pm 6.7$, $B = 10.82 \pm 0.14$, and $A = 1794 \pm 8.4$, $\mu = 8.68 \pm 0.15$, respectively. The ruby pressure scale of [12] in the form (1) is close to our version only up to a pressure of 150 GPa, whereas the scale of [12] in the form (4) almost agrees with our recommendations up to 300 GPa (Fig. 3).

In [13], the ruby pressure scale [1] in the form (3) is proposed: $A = 1845$ GPa, $B = 14.7$, $C = 7.5$. In the pres-

sure range 100–200 GPa, it rather considerably (but still within the limits of 2%) deviates from ours version. It is also necessary to mention the ruby pressure scale reported by Greeff et al. [14]. However, these authors do not provide the analytical form and only remark that their ruby pressure scale is close to the data in [8].

From a comparison of the proposed ruby pressure scale (12) and the scale of Chijioke et al. [12] in the form (4), it is possible to make a conclusion about the most appropriate functional dependence of the R_1 line shift of ruby luminescence on pressure. If one accepts these scales as true, then the scale (12) in the form (2) has a clear advantage, because the parameter $A = 1884$ GPa of this scale is close to the direct measurement of $A = 1875 \pm 30$ GPa [15]. The ruby pressure scale [12] in the form (4) has a considerably smaller value of $A = 1794 \pm 8.4$ GPa, which substantially differs from direct measurements at low pressure [15].

Thus, in the present work we have proposed a new ruby pressure scale based on the the precise measurements of Dewaele et al. [8]. Our calibration of absolute pressure is based on the refined room-temperature isotherms of Al, Au, Cu, Pt, Ta, and W. Our equations of state of these metals are consistent with modern shock-wave data and with numerous thermochemical, X-ray, and ultrasonic measurements of the heat capacity, volume, adiabatic bulk moduli, etc. The obtained ruby pressure scale agrees within 2% with most recent ruby pressure scales [1–4, 8, 12–14], but has a number of advantages. First, it is consistent with the room-temperature isotherms of Al, Au, Cu, Pt, Ta, and W obtained from our unified experiment-based thermodynamic model. Second, the equations of state of Au and Pt agree with the equations of state of Ag and MgO, constructed on independent measurements (see [9]). Third, our scale does not contradict modern equations of state of diamond (see [9]). Fourth, and most important, the results of this work (see the table) contain the complete *PVT* equations of state of Al, Au, Cu, Pt, Ta, and W—thus enabling consistent pressure measurements at any temperature (rather than only at 298 K as with the ruby scale) from the corresponding isotherms of any of these metals.

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