GEOCHEMISTRY

Equations of State of Cu and Ag and Revised Ruby Pressure Scale

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Presented by Academician F.A. Letnikov March 4, 2003

The ruby pressure scale, in which pressure is measured on the basis of R_1 line shift of ruby luminescence, is one of the most widely used pressure standards in experiments with diamond anvil cells for the study of minerals and solid materials under pressure on the room temperature isotherm. To date, the most popular calibration of this pressure scale was that of Mao *et al.* [1], who measured the R_1 line shift of ruby luminescence in an argon medium up to a pressure of 80 GPa. The pressure was determined from room temperature isotherms of Cu and Ag calculated by Carter *et al.* [2] on the basis of shock wave data. This resulted in the wide application of pressure scale expressed as

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

where $A = \lambda(\partial P/\partial \lambda) = 1904$ GPa, $B = 7.665$, and $\lambda_0 = 694.24$ nm.

Almost at the same time, Aleksandrov *et al.* [3] published a significantly different high-pressure scale based on the *a priori* equation of state of diamond. Aleksandrov *et al.* [3] performed simultaneous measurements of the R_1 line shift of ruby luminescence and spectra of the first-order Raman light scattering within a diamond cell in a helium medium up to a compression of $x = V/V_0 = 0.93$. At pressures exceeding 20 GPa, this scale with parameters $A = 1918$ GPa and $B = 11.7$ begins to differ from that suggested by Mao *et al.* [1] and leads to significant differences at pressures greater than 50 GPa (Fig. 1).

Recently, Zha *et al.* [4] measured elastic constants of MgO up to a pressure of 55 GPa using Brillouin scattering. By combining the Brillouin and X-ray measurements, they obtained the equation of MgO state and calculated a new ruby scale with parameters $A = 1904$ GPa

and $B = 7.715$, which agrees with the calibration performed by Mao *et al.* [3] to within 1%.

On the other hand, Holzapfel [5] performed a detailed analysis of modern X-ray, ultrasonic, theoretical, and shock wave data for diamonds and suggested a new ruby scale in the following form:

$$P = \frac{A}{B+C}\left[\exp\left(\left(\frac{B}{C}+1\right)\left(1 - \frac{\lambda}{\lambda_0}\right)^{-C}\right) - 1\right], \qquad (2)$$

where $A = 1820$ GPa, $B = 14$, and $C = 7.3$. The pressures calculated on the basis of this scale fall between the pressure scales of Mao *et al.* [1] and Aleksandrov *et al.* [3] (Fig. 1).

Kalitkin and Kuz'mina [6] suggested an approximation for the global curves of cold compression at pressures from zero to infinity and modified the ruby pressure scale on this basis. Their equations approximated the pressure scale suggested by Mao *et al.* [7], which was obtained at nonhydrostatic conditions. It yields the lowest pressures among all scales shown in Fig. 1.

The first action that should be taken to clarify the causes of this discrepancy is to check the room temperature isotherm of Cu and Ag suggested in Carter *et al.*
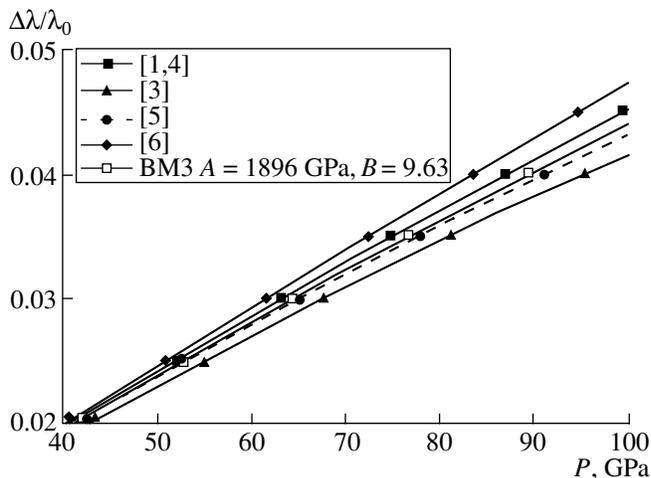
Fig. 1. Ruby pressure standard based on different data.

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[2], which is the basis for the ruby standard calibration by Mao *et al.* [1]. Carter *et al.* [2] calculated these isotherms only on the basis of shock wave data without account for ultrasonic measurements. Since then, the range of shock wave data on Cu and Ag has been significantly widened. In combination with ultrasonic, X-ray, and thermochemical data, this allows us to obtain a reliable equation of state of these metals.

Therefore, the objective of our study is to construct an equation of state of Cu and Ag using modern data and compare the calculated room temperature isotherms with the data of Carter *et al.* [2]. After this, we shall use the data of Mao *et al.* [1] to calculate the volume of Cu and Ag, which would allow us to revise the ruby pressure standard.

THEORETICAL MODEL

The Helmholtz free energy $F(V,T)$ is presented as a sum

$$F(V, T) = U_0 + E(V)$$
$$+ F_{th}(V, T) + F_a(V, T) + F_e(V, T), \qquad (3)$$

where U_0 is the reference energy level, which is introduced to obtain reference values of $\Delta H_{f,\,298}$ and $\Delta G_{f,\,298}$ at standard conditions; $E(V)$ is the potential (cold) part of the free energy at the reference isotherm, which depends only on volume V; $F_{th}(V, T)$ is the thermal part of the free energy, which depends on volume and temperature; $F_a(V, T)$ is the contribution of intrinsic anharmonicity to the free energy, which depends on V and T; and $F_e(V, T)$ determines the contribution of thermal excitation of electrons.

The potential part of the free energy can be taken in any convenient form. Here, we shall use the third-order Birch–Murnaghan equation (BM3) and test the two-parameter approximation suggested by Kalitkin and Kuz'mina [6] (KK2002). The Birch–Murnaghan equation is written in the following form:

$$P(V) = 3fK_0(1 + 2f)^{5/2}(1 + af), \qquad (4)$$

where $f = (x^{-2/3} - 1)/2$, $a = 1.5(K' - 4)$, $x = V/V_0$, V_0, K_0, and K' are volume, shear modulus, and its pressure derivative, respectively, at standard conditions ($T = 298.15$ K, $P = 1$ bar, and $x = 1$).

The Kalitkin–Kuz'mina's equation [6] with two adjusting parameters is written as

$$P(V) = V^{-5/3}(1 - x)\exp(a_0 + a_1(1 - x)), \qquad (5)$$

where $x = (V/V_0)^{1/3}$, a_0 and a_1 are the adjusting parameters.

Let us present the thermal part of the Helmholtz free energy $F(V, T)$ as [8]

$$F_{th} = \sum_1^i m_{Bi} R \left[\frac{d_i + 1}{2d_i} \Theta_{Bi} - T\ln(1 + b_i) \right]$$
$$+ \sum_1^j m_{Ej} R \left[\frac{\Theta_{Ej}}{2} + T\ln\left(1 - \exp\frac{-\Theta_{Ej}}{T}\right) \right], \qquad (6)$$

where Θ_{Bi} is the Bose–Einstein characteristic temperature, Θ_{Ej} is the Einstein temperature, R is the universal gas constant, $b = 1/[\exp(g) - 1]$, $g = d\ln[1 + \Theta_B/(Td)]$, d is the power parameter controlling the heat capacity near 0 K, and m is the number of degrees of freedom. We also require that the sum of the parameters m should be equal to $3n$, where n is equal to the number of atoms in the cell. Usually, at a very good approximation, it is enough to take two Bose–Einstein contributions and two Einstein contributions; i.e., $i = 2$ and $j = 2$.

Let us write the contribution of intrinsic anharmonicity to the Helmholtz free energy in the classical form

$$F_a(V, T) = -3nRaT^2 = -3nRa_0 x^g T^2. \qquad (7)$$

Here, following Zharkov and Kalinin [9], we assumed the simplest dependence of the anharmonicity parameter a on volume: $a = a_0 x^g$. Similarly, we determine the contribution of thermal excitation of electrons:

$$F_e(V, T) = -3nReT^2 = -3Re_0 x^{2/3} T^2. \qquad (8)$$

The volume dependence of the Grüneisen parameter was taken in the following form [10]:

$$\gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)(V/V_0)^\beta = \gamma_\infty + (\gamma_0 - \gamma_\infty)x^\beta, \qquad (9)$$

where γ_∞ and β are adjusting parameters and $\gamma_0 = \alpha V K_T / C_V$ is the Grüneisen parameter at standard conditions.

The pressure on the shock adiabat was calculated using the standard scheme [9]

$$P_H = \frac{P(V) - \dfrac{\gamma}{V}E(V)}{1 - \dfrac{\gamma(1 - x)}{2x}}. \qquad (10)$$

Differentiating Eq. (3) with respect to temperature and volume, we obtain all necessary thermodynamic functions (see [11] for details), which allows us to form a system of equations applicable for the optimization using the weighted least square method. Later, this formalism will be used to construct equations of state of Cu and Ag in a temperature range from 10 K to the melting temperature and a pressure range up to 300 GPa.

EQUATION OF STATE OF Cu AND Ag

Fitted parameters of two models with different cold isotherms for Cu and of the BM3 model for Ag are given in Table 1. The two models for Cu are close to each other and lead to slightly different parameters K'

Adjusting parameters at standard conditions optimizing the thermodynamic properties of Cu and Ag using the BM3 and KK2002 models

Parameters	Cu(1)	Cu(2)	Ag(1)
V_0, cm^3	7.113	7.113	10.272
K_0, GPa	133.9	133.7	100.0
K_{S0}, GPa	137.7*	137.5*	104.0*
K'	5.24	5.40	5.99
$(\partial K_S/\partial P)_T$	5.20*	5.36*	5.90*
$(\partial K_S/\partial P)_S$	5.10*	5.26*	5.75*
Θ_{B1_0}, K	47.24	46.77	120.72
d_1	1.990	1.986	39.325
m_{B1}	0.001	0.001	1.121
Θ_{B2_0}, K	146.57	159.42	112.63
d_2	6.450	6.105	4.266
m_{B2}	0.471	0.578	0.436
Θ_{E1_0}, K	286.65	289.01	191.86
m_{E1}	1.549	1.439	1.443
Θ_{E2_0}, K	181.32	184.97	–
m_{E2}	0.980	0.982	–
γ_0	1.975	1.977	2.439
γ_∞	1.100	1.076	1.655
β	2.722	2.334	5.089
a_0, K^{-1}	–	–	–15.95E-6
g	–	–	6.495
e_0, K^{-1}	10.66E-6	12.24E-6	23.27E-6

Notes: (1) The third-order Birch–Murnaghan equation is used; (2) approximation suggested by Kalitkin and Kuz'mina [6] is used. Asterisk indicates calculations using our models.

and electronic contributions. Here, we do not discuss the real contribution of anharmonicity and the electronic component (both contributions are proportional to T^2 and it is difficult to separate them). Instead, we focus on the most accurate approximation of measured heat capacity and coefficient of thermal expansion. The experimental shock adiabat of Cu was taken from [6] up to a pressure of 300 GPa, and for Ag, from [10] up to 157 GPa. The BM3 model approximates the shock wave data for Cu with a standard deviation of 0.6 GPa, while the deviation is 0.3 GPa for Ag. The KK2002 model gives a standard deviation of 1.3 GPa for Cu.

The deviations of the calculated C_P from the data in [12] do not exceed 1% at temperatures from 10 K to the melting temperature. The deviations of the thermal expansion coefficient α from the data in [13] do not exceed 2% at temperatures above 30 K. The deviations of K_S from the data of Holzapfel et al. [14] are equal to 0.5–1.5% in the entire temperature range for all models. The obtained values $(\partial K_T/\partial P)_T$, $(\partial K_S/\partial P)_T$, and $(\partial K_S/\partial P)_S$ (Table 1) agree with ultrasound data and

slightly exceed the values obtained from the shock wave data [14]. The calculated Grüneisen parameter $\gamma = \alpha V K_T/C_V$ depends on volume and temperature and agrees with the results in [10] and the data in [14] before compression $x = 0.6$. In addition, the calculated standard entropies for Cu in the BM3 and KK2002 models, as well as for Ag in the BM3 model, are equal to 33.13, 33.11, and 42.62 J/(mol K), respectively, which almost coincides with the data from reference handbooks 33.15 ± 0.08 and 42.55 ± 0.21 J/(mol K), respectively.

Thus, we conclude that the equations of state of Cu and Ag obtained here agree with experimental measurements in the temperature and pressure ranges considered here with an error comparable to that of direct measurements. Therefore, we shall further compare the calibration of the ruby pressure standard suggested by Mao et al. [1] with the obtained equations of state for Cu and Ag and the room temperature isotherm from the paper by Carter et al. [2].

REVISED RUBY PRESSURE STANDARD

Using the tables with the data of Carter et al. [2] and Mao et al. [1], it is easy to restore the volume of Cu and Ag given in [1]. Knowing this volume, we calculate the new pressure at given shift of the ruby R_1 line. The difference between newly calculated pressure at the room temperature isotherm and that obtained by Mao et al. [1] from the isotherm given by Carter et al. [2] is shown in Fig. 2. It is seen that the equations of state for Ag based on our data are close to those in [2], while the differences in the equations of state of Cu are significant and reach 2 GPa at a pressure of 70 GPa. Thus, it follows from Fig. 2 that the ruby scale suggested by Mao et al. [1] underestimates pressure at given shift of the ruby R_1 line by a value up to 2 GPa.

The pressures obtained for a given shift of the ruby R_1 line can be approximated by different functions. The following values were obtained for Eq. (1): $A = 1871$ and $B = 10.06$. The third-order Birch–Murnaghan equation yields $A = 1867$ and $B = 10.69$. The Kalitkin–Kuz'mina approximation leads to $A = 1868$ and $B = 10.43$. The ruby R_1 line shift as a function of pressure calculated from the third-order Birch–Murnaghan equation with parameters $A = 1896$ and $B = 9.63$ is shown in Fig. 1. In this case, parameter A was fixed according to the initial slope under hydrostatic conditions [15]. The obtained dependence of the ruby R_1 line shift on pressure gives the average pressure that is halfway between the scale suggested by Mao et al. [1] and independent scale suggested by Holzapfel [5].

Conclusions. We constructed the equations of state of Cu and Ag, which agree with the shock wave, ultrasonic, X-ray, and thermochemical data in a temperature range from 10–20 K to the melting temperature and to compression $x = 0.6$. The comparison of the calculated room temperature isotherm with that recommended by

$P_{cal} - P_{exp}$, GPa
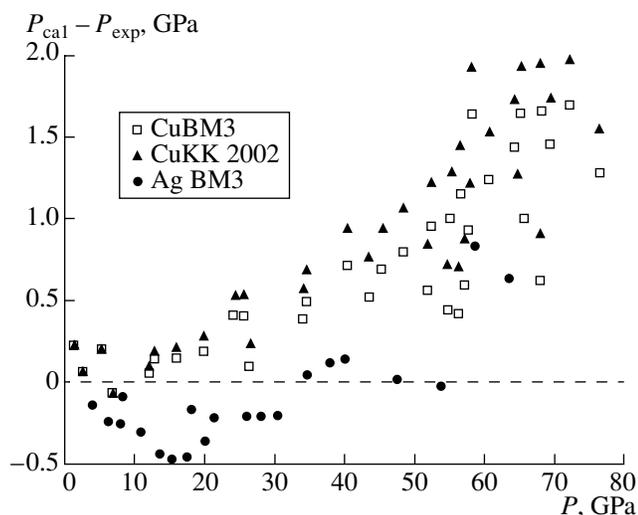
Fig. 2. Deviations of ruby pressure standard based on the suggested equations of state of Cu and Ag from the pressure scale recommended by Mao *et al.* [1].

Carter *et al.* [2] revealed that the latter deviates from our version by a value up to 2 GPa at a pressure of 70 GPa, which leads to a systematic error in the ruby pressure standard suggested by Mao *et al.* [1]. We recommend a new pressure scale of ruby R_1 line shift dependence on pressure, which yields the pressures intermediate between the values given by Mao *et al.* [1] and the independent scale suggested by Holzapfel [5]. Hence, it is necessary to revise the equations of state for minerals obtained on the basis of the ruby standard suggested by Mao *et al.* [1].

ACKNOWLEDGMENTS

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