Ruby pressure scale: revision and alternatives

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Summary
We have constructed semi-empirical equations of state of Al, Au, Cu, Pt, Ta, and W, which agree within experimental error bars with the shock wave, ultrasonic, X-ray, and thermochemical data in a temperature range from 10-20 K to melting temperature and to compression $x=V/V_0=0.5-0.6$. The comparison of the calculated room isotherms for these metals with quasi-hydrostatic measurements of Dewaele et al. (2004a, b) supports recently proposed ruby pressure scales (Holzapfel, 2003; Dorogokupets and Oganov, 2003; Dewaele et al., 2004b). We recommend a new ruby pressure scale in the form $P = A(\Delta \lambda / \lambda_0)(1 + B\Delta \lambda / \lambda_0)$ with parameters $A=1884 \text{ GPa}$ and $B=11$. The cross analysis on independent data of Akahama et al. (2002; 2004), Sata et al. (2002), Matsui and Nishiyama (2003), Nishiyama et al. (2004), Fei et al. (2004a, b) confirms the resulting equations of state of Al, Au, Cu, Pt, Ta, W, Ag, MgO, and diamond, whose room-temperature isotherms can be used as an alternative for the ruby pressure scale.

Introduction
The ruby pressure scale, in which pressure is measured on the basis of the $R_1$ line shift of ruby luminescence, is one of the most widespread standards of pressure in experiments with diamond anvils cells at room temperatures and pressures up to ~1 Mbar. It is a secondary pressure scale, therefore it requires a careful calibration. Until now the most popular calibration was that of Mao et al. (1986), which was based on the measurements of the $R_1$ line shift of ruby luminescence in argon medium up to the pressure of 80 GPa. The pressure was determined from room-temperature isotherm of Cu and Ag calculated by Carter et al. (1971) from shock wave data. The initial slope of $P(\lambda)$ has been accepted from Piermarini et al. (1975) measurements and is $A=\lambda(\partial P/\partial \lambda)=1904 \text{ GPa}$. This value has been obtained by Piermarini et al. (1975) with the use of Decker’s (1971) EoS of NaCl as pressure standard in quasi-hydrostatic medium (up to 10.4 GPa) and in non-hydrostatic medium up to the pressure of 20 GPa. This resulted in the wide application of ruby pressure scale expressed as (Mao et al., 1986):

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

$$P = \frac{A}{B}[(\lambda/\lambda_0)^B - 1] \quad (1a)$$

where $B=7.665$, $\lambda_0=694.24 \text{ nm}$ (Piermarini et al., 1975).

Almost at the same time, Aleksandrov et al. (1987) published a significantly different high-pressure ruby scale based on the $a priori$ equation of state of diamond. Aleksandrov et al. (1987) 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, the scale of Aleksandrov et al. (1987) with parameters $A=1918 \text{ GPa}$ and $B=11.7$ for equation 1 and with parameters $A=1892\pm13 \text{ GPa}$ and $m=6.4\pm0.5$ or $B=12.8$ for equation 2 begins to differ from that suggested by Mao et al. (1986) and leads to significant differences at pressures greater than 50 GPa (Fig. 1).

$$P = A(\Delta \lambda / \lambda_0)(1 + m\Delta \lambda / \lambda_0), \quad (2)$$
Hemley et al. (1989) have obtained the equation of state of solid neon up to 110 GPa using the ruby (Mao et al., 1986) and tungsten (McQueen et al., 1970) pressure scales and overall have confirmed the calibration of Mao et al. (1986) for the ruby pressure scale. However, they emphasize that the tungsten pressures are systematically higher than the predictions of the ruby scale at higher pressures, but this difference is within the expected error in the tungsten isotherm (Hemley et al., 1989, p. 11822). Further, they noticed that compressed solid helium remains considerably weaker than neon and argon at high pressure (Bell and Mao, 1981). Therefore, in the opinion of Hemley et al. (1989), part of contradictions between Aleksandrov et al. (1987) and Mao et al. (1986) pressure scales may be associated with residual nonhydrostatic effects in the heavier rare-gas media.

Recently, Zha et al. (2000) measured elastic constants of MgO up to the 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 \( A = 1904 \text{ GPa} \) and \( B = 7.715 \), which agrees with the calibration performed by Mao et al. [3] to within 2%.

However, a series of works (Holzapfel, 2003; 2005; Dorogokupets and Oganov, 2003; Kunc et al., 2003; Dewaele et al., 2004b) was recently published, in which Mao et al. (1986) ruby pressure scale has been essentially shifted towards the ruby pressure scale of Aleksandrov et al. (1987) (Fig. 1).

The ruby pressure scale proposed by Holzapfel (2003), which was based on a comparison of
modern high pressure X-ray diffraction data for diamond and tantalum with low-pressure ultrasonic data, shows a significant difference from scales Mao et al. (1978; 1986) and comes nearer to the scale of Aleksandrov et al. (1987). The scale of Holzapfel (2003) has the following form:

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

where $A=1820$ GPa, $B=14$, $C=7.3$ and corresponds to eq. (1) in the limit of $C \to 0$.

Dorogokupets and Oganov (2003) have constructed the equations of state of copper and silver, which agree with experimental measurements in the temperature range from 10-20 K up to the melting temperature and up to the compression $x=0.6$, and have obtained a ruby pressure scale, which may be approximated by different functions. For the third-order Birch-Murnaghan equation they have obtained parameters $A=1896$ GPa and $B=9.63$, for equation (1) these parameters are $A=1871$ GPa and $B=10.06$. These scales agree quite well with the ruby pressure scale of Holzapfel (2003) up to 100 GPa, but at higher pressure the difference between them is non-negligible (Fig. 1).

Kunc et al. (2003) have compared the theoretical equation of state of diamond with high-quality data of Occelli et al. (2003), which have carried out X-ray diffraction measurements of diamond with helium pressure transmitting medium in diamond-anvil cells (DAC). However, Occelli et al. (2003) obtained the value $dK/dP =3.0\pm0.1$ using the ruby scale of Mao et al. (1986), and this value appeared too low in comparison with the value from ultrasonic measurements $dK/dP =4\pm0.5$ (McSkimmin and Andreatch, 1972) and theoretical data of Kunc et al. (2003) $dK/dP =3.65\pm0.05$. Kunc et al. (2003) have assumed, that the discrepancy between experimental and calculated EoS and phonon frequency results for diamond are caused by some error in Mao et al (1986) ruby pressure scale. To remove the discrepancy for the phonon frequency, Kunc et al. (2003) have proposed a revised ruby scale in the form (2a) with parameters $A=1820$ GPa (fixed value as recommended Holzapfel (2003)) and $B=15.8$.

For calibration of the ruby pressure scale, it is necessary to recognize as revolutionary the work of Dewaele et al. (2004b), where $PV$ relations at room temperature have been measured for Ta, Au, and Pt to 94 GPa and for Al, Cu, and W to 153 GPa in diamond anvil cells with helium pressure-transmitting medium. When they have compared the equations of state of these metals based on the ruby scale of Mao et al. (1986) and the room-temperature isotherms obtained from reducing shock-wave data (Hixon and Fritz, 1992; Wang et al., 2002), it appeared that they differ by up to 8-9 GPa at pressures of 100-150 GPa. In result, they have obtained a ruby pressure scale with parameters $A=1904$ GPa and $B=9.5$. This scale give practically the same pressures as scales of Holzapfel (2003) and of Dorogokupets and Oganov (2003).

On the Third meeting on the Study of Matter at Extreme Conditions (SMEC 2005), 17-21 April of 2005 (Miami Beach, Florida) several reports have been dedicated to derivation of pressure standards. In particular, Chijioke et al. (2005) have compared experimental $PV$ measurements and the shock data for different materials and have obtained a new ruby scale with parameters $A=1873.4\pm6.7$ GPa and $B=10.82\pm0.14$ for the equation (1.) Greef et al. (2005) have carried out the analysis of the equations of state of Cu, Au, and Pt and have confirmed the ruby pressure scale of Dewaele et al. (2004b).

Holzapfel (2005) has reconsidered Dewaele et al. (2004b) and Occelli et al (2003) data and has obtained a ruby pressure scale with parameters $A=1845$ GPa, $B=14.7$, $C=7.5$ for eq. (3), which rather considerably differs from previous (Holzapfel, 2003) ruby pressure scale (Fig. 1).

Thus, results of studies of last years unequivocally show, that the Mao et al. (1986) ruby pressure scale requires a significant correction. However there were contradictions between ruby pressure scale based on studies diamond (Aleksandrov et al., 1987; Kunc et al., 2003),
and on the basis of the equations of state of metals (Dorogokupets and Oganov, 2003; Dewaele et al., 2004b, Chijioke et al., 2005; Greef et al., 2005), and also of diamond and tantalum (Holzapfel, 2003) (Fig. 1).

Therefore in the present work we shall consider semi-empirical equations of state of Al, Au, Cu, Pt, Ta, and W for the temperature range from 10-15 K to the melting temperature and up to pressures 200-300 GPa (or, up to compression $x=V/V_0=0.5–0.6$), and we shall show that they agree with experimental measurements of the heat capacity, thermal expansion coefficient, adiabatic bulk modulus at atmospheric pressure, and also with the data from the Shock Wave Data Base (SWDB, Khishchenko et al., 2001). Further we compare the calculated room-temperature isotherms for these metals with quasihydrostatic data of Dewaele et al. (2004a, b), that will allow us to obtain a new ruby pressure scale. Based on the newly obtained ruby pressure scale, we shall carry out a careful analysis of different analytical forms of $P=f(\lambda)$, and we shall show that the form (1) is valid for pressures below 100 GPa. Then we shall consider equations of state of Ag, MgO and diamond and we shall carry out a cross-check of the obtained equations of state and the ruby pressure scale on independent data, which will allow us to obtain the equations of state, which are consistent with each other and with the ruby pressure scale. As a basis of construction of the equation of state we will use the expanded formalism of Dorogokupets and Oganov (2003).

**Thermodynamics**

Let us write the Helmholtz free energy $F(V, T)$ as the sum (Zharkov and Kalinin, 1972):

$$F = U_0 + E(V) + F_{\text{th}}(V, T) + F_{\text{anh}}(V, T) + F_{\text{el}}(V, T) + F_{\text{def}}(V, T),$$

(4)

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

Differentiating (4) with respect to temperature at constant volume and with respect to volume at constant temperature, we obtain all necessary thermodynamic functions: entropy, $S = -\langle cF \partial T \rangle_V$, internal energy $E=F+TS$, heat capacity at constant volume, $C_V = \langle cE \partial T \rangle_V$, pressure, $P = -\langle cF \partial V \rangle_T$, isothermal bulk modulus, $K_T = -\langle cP \partial V \rangle_T$, slope of pressure at constant volume ($\langle cP \partial V \rangle_V = \alpha K_T$, where $\alpha = 1/\langle cV \partial T \rangle_P$). Heat capacity at constant pressure is $C_P=C_V+\alpha^2 TK_V$, adiabatic bulk modulus is $K_\theta=K_T+VT(T(\alpha K_T)^2/C_V)$. Enthalpy and Gibbs free energy can be found from $H=E+PV$, $G=F+PV$. For the account of the shock wave data we use the Rankine–Hugoniot relations. Now it is necessary to define the analytical forms of functions in (4).

Cold energy and pressure are written as (Vinet et al., 1987):

$$E(V) = 9K_0V_0\eta^{-2} [1 - (1 - \eta(1-y))] \exp[(1-y)\eta] ,$$

(5)

$$P(V) = -\langle cE \partial V \rangle_V = 3K_0V^{-2}(1-y)\exp[(1-y)\eta] ,$$

(5a)

where $y=x^{1/3}$ and $\eta=1.5 (K'-1)$.

The greatest complexity is associated with the approximation of the thermal part of the Helmholtz free energy through the whole range of temperatures, and we shall use therefore the formalism of Kut'lin et al. (Kut'lin and Pyadushkin, 1998; Kut'lin et al. 1998), who represented the Gibbs free energy in the Bose–Einstein form:

$$G = -m_BRT \ln(1 + b),$$

(6)

where $R$ is the gas constant, $m_B$ is the number of degrees of freedom ($m_B=3n$, where $n$ is number of atoms in a cell); $b=1/[\exp(g)-1]$, $g=dn[1+\Theta_B/Td]$, $d$ is the exponential parameter controlling the behavior of the heat capacity near 0 K, $\Theta_B$ is the characteristic temperature. These authors noticed that this analytical approximation yields both a $C_V \sim T^3$ dependence of
the heat capacity at low temperatures and constant limit (7) at high temperatures. By differentiation of (6) with respect to temperature, one can easily obtain the entropy, enthalpy and heat capacity. Kut'in et al. (Kut'in and Pyadushkin, 1998; Kut'in et al. 1998) have shown, that the equation (6) in combination with the Einstein energy

\[ G = -m_BRT \ln(1 + b) + m_ERT \ln \left( 1 - \exp \left( -\frac{\Theta_E}{T} \right) \right) \]  

approximates well thermodynamic functions from 0 K up to the ambient temperature.

This formalism can be used for analytical representation of the thermal part of the Helmholtz free energy, which can be written as:

\[ F_{th} = \sum_i \frac{m_{Bi}}{R} \left[ \frac{(d_i - 1)}{2d_i} \Theta_{Bi} - T \ln(1 + b_i) \right] + \sum_i \frac{m_{Ei}}{2} \left[ \Theta_{Ei}^2 + T \ln(1 - \exp \left( -\frac{\Theta_{Ei}}{T} \right)) \right], \]  

where \( \Theta_{Bi} \) is the Bose-Einstein characteristic temperature, \( \Theta_{Ei} \) is the Einstein characteristic temperature. Usually for a very accurate approximation it is enough to take two Bose-Einstein contributions (8) and two Einstein contributions, i.e. \( i = 2 \) and \( j = 2 \).

For the volume dependence of the Grüneisen parameter we used the Al'tshuler et al. (1987) equation:

\[ \gamma = \gamma_\infty + (\gamma_0 - \gamma_\infty)(V/V_0)^\beta = \gamma_\infty + (\gamma_0 - \gamma_\infty)x^\beta, \]  

where \( \gamma_0 \) is the Grüneisen parameter at ambient conditions, \( \gamma_\infty \) is the Grüneisen parameter at \( x=0 \) and \( \beta \) is a fitted parameter. When data are not sufficient to determine all these parameters, parameter \( \beta \) can be taken as \( \beta = \gamma_0/(\gamma_0 - \gamma_\infty) \) (Al'tshuler et al., 1987). From (9) it is possible to calculate the volume dependence of the characteristic temperatures and parameter \( q \):

\[ \Theta = \Theta_0 x^{-\gamma_\infty} \exp \left[ \frac{\gamma_0 - \gamma_\infty}{\beta} (1 - x^\beta) \right]. \]  

The form (9), apart from its mathematical simplicity and convenience, has a correct behaviour at infinite compression (\( \gamma \rightarrow \text{constant}, \ q \rightarrow 0 \)) and agrees with results of theoretical calculations.

The intrinsic anharmonicity contribution to the Helmholtz free energy is approximated in the Oganov and Dorogokupets (2004) formulation:

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

The electronic component of the Helmholtz free energy is taken as:

\[ F_{el} = -\frac{3}{2} nR \exp \left( \frac{gT^2}{2} \right). \]  

where \( g=2/3 \).

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

\[ F_{def} = -\frac{3}{2} nRT \exp \left( Sx^f - \frac{Hx^h}{T} \right), \]
where \( S, H, f, h \) are fitted parameters, but the latter two parameters were fixed for all metals: \( f = -1, h = -2 \) excluding tantalum \((h = -4 \) after Mukherjee et al., 2003).

The resulting equation of state allows to carry out a simultaneous processing of all available measurements of the heat capacity, thermal expansion coefficient, volume and adiabatic and isothermal bulk moduli at zero pressure, static measurements of volume on a room-temperature isotherm and at higher temperatures, shock wave data, and to calculate any thermodynamic functions of pressure, temperature, and volume.

**Results**

If the obtained equation of state is considered only in the thermodynamic sense, then all the fitted parameters can be obtained from a simultaneous processing of experimental data for \( C_p, \alpha, V, K_S \) at zero pressure and shock wave data. It is necessary to emphasize, that we did not involve ultrasonic measurements \( dK_S/dP \) during the analysis of experimental data. Values \( dK/dP \) in Table 1 are obtained as fitted parameters among others, approximating experimental temperature dependence of the adiabatic bulk modulus at zero pressure.

Originally such analysis has been carried out for Al, Cu, Ta, and W, for which the values of \( K_0 \) and \( dK/dP \) equal to 73.46 GPa and 4.52, 133.98 GPa and 5.41, 191.44 GPa and 3.93, 306.23 GPa and 4.16 at ambient conditions have been obtained, and this results in a catastrophic divergence from the data of Dewaele et al. (2004b) above 30 GPa if the Mao et al (1986) ruby pressure scale is used (Fig. 2A).

![Graph A](image)

**Fig. 2. A.** Difference between the Dewaele et al. (2004a, b) pressure using the Mao et al. (1986) ruby scale and our calculated room-temperature isotherms for Cu, Al, Ta, and W. **B.** Difference from the Dewaele et al. (2004b) pressure using the ruby scale with parameters \( A=1885 \) GPa and \( B=10.4 \) for eq. (1).
From the equations of state of these metals using eq. (1) the preliminary ruby pressure scale with parameters $A=1885$ GPa and $B=10.4$ has been obtained. Parameter $A$ has been fixed as the average of Piermarini et al. (1975) data for quasihydrostatic conditions ($A=1896$ GPa (Dorogokupets, Oganov, 2003)) and direct definitions $A=1875\pm 30$ GPa (Grasset, 2001). Using this pressure scale and Dewaele et al. (2004b) measurements, the equations of state for Au and Pt have been obtained. The differences from Dewaele et al. (2004b) pressure using ruby pressure scale with parameters $A=1885$ GPa and $B=10.4$ for eq. (1) are shown in Fig. 2B. It would seem possible to consider this result as satisfactory and stop the analysis here, since the errors do not exceed 2 GPa, i.e. less than 2-3 %, however in a Fig. 2B we can see a minimum of deviations in the field of 70-120 GPa. If one assumes that the experimental measurements of Dewaele et al. (2004b) are absolutely reliable, then it is necessary to continue the analysis.

<table>
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<th>Parameter</th>
<th>Al</th>
<th>Au</th>
<th>Cu</th>
<th>Pt</th>
<th>Ta</th>
<th>W</th>
<th>C</th>
<th>MgO</th>
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* $V_0$ are from Robie et al (1978). ** Fitted values of the coefficient $e$ are smaller than or equal to those derived from low-temperature heat capacity measurements.

Therefore, we consider two possible causes of this minimum:

1) Phase transitions of ruby at these pressure (Funamori & Jeanloz, 1997; Mashimo et al., 2000; Lin et al., 2004; Caracas & Cohen, 2005; Oganov and Ono (submitted)) could affect the dependence $P(\lambda)$.

2) Functional dependence (1) is not suitable for extrapolation in the high-pressures region.
Therefore we have carried out an additional analysis of the equations of state of all six metals up to pressure 100 GPa (fitting parameters are listed in Table 1) and have obtained a new ruby pressure scale with parameters $A=1885$ GPa and $B=11$ (eq. 1), which very well agrees with the data of Dewaele et al (2004b) up to the pressure of 100 GPa (Fig. 3). However, at pressures higher than 100 GPa we have regular deviations up to 5 GPa from the measurements of Dewaele et al (2004b) for Al, Cu, and W, which could be a measure of the effect of phase transitions in ruby on $P(\lambda)$.

If the first assumption is true, then we need in two ruby pressure scales: first with parameters $A=1885$ GPa and $B=11$ (eq. 1) up to pressure 85 GPa, the second scale should have parameters $A=1975$ GPa and $B=8.59$ (eq. 1) in the region above 85 GPa.

However if to assume, that at static compression at room temperature ruby will keep its
structure in the metastable state, then a search of an alternative functional form may be needed for the ruby pressure scale. One could use the Holzapfel (2003) equation in the form (3), however the best results are obtained with the equation (15):

$$P = 1884 \times \left( \frac{\Delta \lambda}{\lambda_0} \right) \left( 1 + \frac{11}{2} \frac{\Delta \lambda}{\lambda_0} \right).$$  \hspace{1cm} (15)

Now the deviations of the calculated room-temperature isotherms from Dewaele et al. (2004b) data are only slightly in excess of 1 GPa at pressures up to 160 GPa (Fig. 4).

Fig. 5. Comparison of calibration curves of the wavelength of the ruby R1 luminescent line at pressures 50-100 GPa (A) and 100-160 GPa (B). Black lines are calculated with eq. (1), red lines calculated with eq. (2). Black rectangles are pressures calculated using the Holzapfel (2003), Dorogokupets and Oganov (2003) and Dewaele et al. (2004b) ruby pressure scales. Aleksandrov et al. (1987) ruby pressure scale it is shown in two variants for the equations (1) and (2).
Fig. 6. Comparison of thermodynamic functions of gold calculated from our EoS (parameters from Table 1) with various experimental and theoretical data. A – heat capacity at constant pressure and constant volume. B – deviations of calculated low temperature heat capacity from experimental measurements in %. C – thermal expansion coefficient. D – bulk moduli. E – deviations of calculated pressure with experimental and theoretical data. F – calculated 300 and 1500 K isotherms and shock adiabats in comparison with experiments. G – Gruneisen parameters. H – calculated shock wave velocity versus particle velocity in comparison with Shock Wave Data Base (Khishchenko et al 2001).
In a Fig. 5 are shown primary and recalculated Mao (1986) data for copper and recalculated data of Dewaele et al. (2004a, b) for six metals using the ruby pressure scale in the form (15), at pressures pressure 50-100 GPa (A) and 100-155 GPa (B).

Thus, we have obtained two variants of the ruby pressure scale with different functional dependences $P(\lambda)$ which give identical pressure up to 160 GPa. In a final version we prefer the equation (15) which has the form proposed by Aleksandrov et al. (1987) and justified on the example of diamond by Kunc et al. (2003).

We conclude that the equations of state of Al, Au, Cu, Pt, Ta and W obtained here agree with experimental measurements in the temperature and pressure ranges considered here with an error comparable to that of direct measurements (comparison calculated and experimental thermodynamic functions are shown in Fig. 6 for the case of gold). Hence, one can expect that the obtained equations of state will be correct at higher temperatures and pressure. This statement will be confirmed in the following section by comparison of the equations of state of gold, platinum, silver and MgO.

Besides, as we stated in the Introduction, the ruby pressure scales based on equations of state of metals and on the equations of state of diamond are significantly different. Therefore we have constructed the equation of state of diamond using recalculated Occelli et al. (2003) room-temperature isotherm, and experimental measurements of $C_P$, $\alpha$, $K_S$. The obtained value $dK/dP=3.72$ (Table 1) turns out to be close to the results of Kunc et al. (2003) and coincides with results of ab initio calculations (Oganov, unpublished).

**Discussion**

In this section we shall perform a cross-check of the obtained equations of state using additional independent data. Akahama et al. (2002) have measured simultaneously the unit cell parameters of bismuth, platinum and gold in nonhydrostatic conditions on the room-temperature isotherm. Using the equation of state of platinum of Holmes et al. (1989), Akahama et al. (2002) have obtained a room-temperature isotherm of gold ($K_0=166.3$ GPa, $dK/dP=6.24$) which agree with our results and those of Holzapfel et al. (2001). It is not surprising, as the equation of state of platinum of Holmes et al. (1989) agrees within 1 GPa with our calculation. The deviations of the gold pressure scale from the platinum scale (Table 1), calculated from our data and the data of Dewaele et al. (2004b), computed using the equation of state of bismuth (Akahama et al., 2002), are shown in a Fig. 7A.

**Fig. 7.** A. Difference between Au and Pt pressure scale calculated with our (Table 1) and Dewaele et al. (2004b) data using the equation of state of bismuth of Akahama et al. (2002.) B. Difference between Au and Ag pressure scales calculated with our data (Table 1) using Akahama et al. (2004) measurements.

Later Akahama et al. (2004) have measured simultaneously the cell parameters of silver and gold in nonhydrostatic conditions. The difference between Au and Ag pressure scales calculated with our data (Table 1) using Akahama et al. (2004) measurements is shown in Fig. 7B.
Sata et al. (2002) at studies of pressure-volume relations of the high-pressure B2 phase of NaCl used the equations of state of platinum (Holmes et al., 1989) and MgO (Speziale et al., 2001) as pressure scales. The difference between pressure on MgO and Pt on data Sata et al. (2002) and on our equations of a condition is shown in a Fig. 8.

![Fig. 8. Difference between MgO and Pt pressure scale on the room-temperature isotherm calculated with our equations of state (red symbols) and with equations of state of Speziale et al. (2001) and Holmes et al. (1989).](image)

The self-consistency of our equations of state can be checked not only on room-temperature isotherms, but also at higher temperatures and pressures on the example of the PVT measurements of the unit cell parameters of MgO, Pt, and Au by Matsui and Nishiyama (2003), Nishiyama et al. (2004) and Fei et al. (2004a, b). Using the measured cell parameters we have calculated pressures for these materials at different temperatures. Fig. 9 compares the pressure scales of MgO and Au (A), and Pt and Au (B). Values of temperatures with a symbol "a" correspond to Fei et al. (2004a) data, with a symbol "b" Fei et al. (2004b) data.

![Fig. 9. A. Difference between MgO and Au pressure scale calculated with our EoS (Table 1) using Fei et al. (2004a, b) measurements at different temperatures, Matsui and Nishiyama (2003) and Nishiyama et al. (2004) measurements at 1873 K. B. Difference between Pt and Au pressure scales calculated with our EoS (Table 1) using Fei et al. (2004a, b) measurements at different temperatures.](image)
In summary we would like to make some remarks about the difference between existing scales at pressure up to 300 GPa and influence on them of the form of dependence $P(\lambda)$ (see Fig. 10). At given value $\lambda$ we have calculated pressure using known ruby pressure scales and deviations of this pressure from our scale in the form (15). The scatter of calculated pressures between the first and the latter scales exceeds ±30 GPa at pressure 300 GPa. If one examines the ruby pressure scales published after 2003, then the difference between them is greatly reduced except for Kunc et al (2003) scale, which, however, has been constructed only on diamond. At pressure 150 GPa the modern scales approximated by various functional dependences, will be consistent within the bounds of ±4 GPa, and at higher pressures they begin to diverge. It is obvious that such difference is related to different forms of $P(\lambda)$, which is easily seen in the example of our scale in the form eq. (1) with parameters $A=1885$ GPa and $B=11$ (see Fig. 4 and 5B) which as we marked, is good up to pressure 85 GPa, and above 85 GPa has parameters $A=1975$ GPa and $B=8.59$. This scale has designation as DO eq 1. Chijioke et al (2005) scale in the form eq. (1) at pressure above 100 GPa considerably deviates from our equation (15), however the difference immediately decreases up to 3 GPa at 300 GPa when the functional form (2) is used. Deviations of the three-parametrical ruby pressure scale of Holzapfel (2005) have a minimum in the region 150-200 GPa, and will be consistent with our scale (15) at 300 GPa. Thus, the functional dependence (2) is quite sufficient for approximation of the ruby pressure scale up to 300 GPa.

**Concluding remarks**

We have obtained internally consistent semi-empirical equations of state of Al, Au, Cu, Pt, Ta, W, Ag, MgO, and diamond for a wide range of temperatures and pressure on the basis of a simultaneous analysis of the thermochemical, X-ray, ultrasonic and shock wave data.
Comparison of the calculated room-temperature isotherms of these metals with static VP measurements of Dewaele et al. (2004b) has allowed us to reconsider the calibration of the Mao et al. (1986) ruby pressure scale. The revised ruby pressure scale has a simple functional form proposed by Aleksandrov et al. (1987), which is capable of approximating the obtained $P(\lambda)$ dependence in the whole pressure range 0-300 GPa by one equation, unlike the functional form of Mao et al. (1986). The cross-check of the independent data of Akahama et al. (2002; 2004), Sata et al. (2002), Matsui and Nishiyama (2003), Nishiyama et al. (2004), Fei et al. (2004a, b) confirms the obtained equations of state of Al, Au, Cu, Pt, Ta, W, Ag, MgO, and diamond. Room-temperature isotherms of these materials can be an alternative to the ruby pressure scale.

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