

2.7. HIGH-PRESSURE DEVICES

Table 2.7.2

Luminescence pressure sensors, their electronic transition types (s = singlet, d = doublet) and rates of spectral shifts (after Holzapfel, 1997)

Sensor	Transition	λ_0 (Å)	$d\lambda/dP$ (Å GPa ⁻¹)	$d\lambda/dT$ ($\times 10^{-2}$ Å K ⁻¹)	$(d\lambda/dP)/\Gamma$ (Å GPa ⁻¹)	$(d\lambda/dT)/(d\lambda/dP)$ ($\times 10^{-2}$ GPa K ⁻¹)
Cr ³⁺ :Al ₂ O ₃	² E _g ⁴ A ₂ /d	6942	3.65 (9)	6.2 (3)	4.9	17.0
Sm ²⁺ :SrB ₄ O ₇	⁵ D ₀ ⁷ F ₀ /s	6854	2.55	-0.1	17.0	-0.4
Sm ²⁺ :BaFCl	⁵ D ₀ ⁷ F ₀ /s	6876	11.0	-1.6	4.8	-1.5
Sm ²⁺ :SrFCl	⁵ D ₀ ⁷ F ₀ /s	6903	11.2 (3)	-2.36 (3)	5.8	-2.1
Eu ³⁺ :LaOCl	⁵ D ₀ ⁷ F ₀ /s	5787	2.5	-0.5	1.0	-2.0
Eu ³⁺ :YAG	⁵ D ₀ ⁷ F ₁ /d	5906	1.97	-0.5	0.7	-2.5

Table 2.7.3

Parameters recommended for pressure determination by EOS measurements

Various face-centred cubic (f.c.c.) and body-centred cubic (b.c.c.) metals are used as calibrants, with the EOS given by equation (2.7.1) and the reference temperature $T_R = 300$ K (after Holzapfel, 1997).

Metal	a_{0R} (pm)	K_{0R} (GPa)	K'_{0R}	α_{0R} ($\times 10^6$ K)	$\delta_{\alpha R}$
Al	404.98 (1)	72.5 (4)	4.8 (2)	23.0 (4)	5.5 (11)
Cu	361.55 (1)	133.2 (2)	5.4 (2)	16.6 (3)	6.1 (6)
Ag	408.62 (1)	101.0 (2)	6.2 (2)	19.2 (4)	7.1 (6)
Au	407.84 (1)	166.7 (2)	6.3 (2)	14.2 (2)	7.2 (6)
Pd	388.99 (1)	189 (3)	5.3 (2)	11.6 (4)	6.0 (11)
Pt	392.32 (1)	277 (5)	5.2 (2)	8.9 (4)	5.9 (11)
Mo	314.73 (1)	261 (5)	4.5 (5)	5.0 (4)	5.2 (14)
W	316.47 (1)	308 (2)	4.0 (2)	4.5 (4)	4.7 (11)

Table 2.7.4

Pressure fixed points at ambient temperature (after Holzapfel, 1997; Hall, 1980)

P (GPa)	Element transition
0.7569 (2)†	Hg freezing at 273 K
1.2 (1)†	Hg freezing at 298 K
2.55 (6)†	Bi I–II at 298 K
3.67 (3)†	Tl h.c.p.–f.c.c.
2.40 (10)†	Cs I–II
4.25 (1)†	Cs II–III
4.30 (1)†	Cs III–IV
5.5 (1)‡	Ba I–II
7.7 (2)‡	Bi III–IV
9.4 (3)†	Sn I–II
12.3 (5)†	Ba II–III
13.4 (6)†	Pb I–II

† Onset of forward transition. ‡ Centre of hysteresis.

$$P = 1904[(\lambda/\lambda_0)^B - 1]/B,$$

where $B = 7.665$ for quasi-hydrostatic and 5.0 for non-hydrostatic conditions (Mao *et al.*, 1986, 1978; Bell *et al.*, 1986).

The ruby fluorescence depends strongly on temperature (Barnett *et al.*, 1973; Vos & Schouten, 1991; Yamaoka *et al.*, 2012) and a temperature change of about 6 K causes R_1 line shifts equivalent to 0.1 GPa. The fluorescence-line dependence on temperature is much weaker for Sm²⁺:SrB₄O₇ (Lacame & Chateau, 1989; Lacame, 1990; Datchi *et al.*, 1997) and the other rare-earth-doped sensors listed in Table 2.7.2. These sensors can be more sensitive to pressure than ruby, and together with ruby can be used simultaneously for both temperature and pressure calibration.

The calibration of most pressure gauges is based on comparisons of theoretical and shock-wave data (Holzapfel, 1997), so the derived equations of state are used with an accuracy of about 5% up to 1 TPa. The EOS recommended by Holzapfel (1997) is

$$P = [3K_0(1-x)/x^5] \exp[c_0(1-x)], \quad (2.7.1)$$

where $x = a/a_0 = (V/V_0)^{1/3}$, $c_0 = 3(K_0' - 3)/2$, a is the unit-cell dimension, V is the unit-cell volume, a_{0R} and V_{0R} are the reference parameters under ambient conditions (Table 2.7.3), α_{0R} is the thermal expansion coefficient, K_{0R} is the bulk modulus, and $K_0' = dK_0/dP$. $dK_0/dT = -3\alpha_{0R}K_0\delta_{\alpha R}$, where $\delta_{\alpha R} = \partial(\ln\alpha)/\partial(\ln V)_{T_R}$. Pressure can be computed by assuming constant K_0' and linear temperature relations for T close to or higher than $T_R = 300$ K:

$$a_0(T) = a_{0R}[1 + \alpha_{0R}(T - T_R)],$$

$$V_0(T) = V_{0R}[1 + 3\alpha_{0R}(T - T_R)],$$

$$K_0(T) = K_{0R}[1 - \alpha_{0R}\delta_{\alpha R}(T - T_R)].$$

The details of the parameterization are explained by Holzapfel (1991, 1994) and listed for the simple face-centred (f.c.c.) and body-centred (b.c.c.) cubic metals in Table 2.7.3 (Holzapfel, 1997). Powders of these metals can be mixed with the sample and its pressure can be calibrated according to the unit-cell dimension of the standard. The well known compressibilities of NaCl, CaF₂ and MgO, in the form of either powders or single crystals, are also often used as internal pressure standards (Dorfman *et al.*, 2010, 2012; Dorogokupets & Dewaele, 2007).

An independent pressure assessment can be obtained from standard materials undergoing pressure-induced phase transitions (Table 2.7.4). This method is limited to just a few pressure points (Holzapfel, 1997), but they can provide a useful verification of other pressure gauges.

Other methods of pressure calibration are still being developed. For example, it has been shown that very high pressure can be determined from the Raman shift of strained diamond-anvil culets (Akahama & Kawamura, 2004). The strong piezochromic effect of visible colour changes in soft coordination polymers allows pressure calibration without spectrometers. These changes can proceed gradually (Andrzejewski & Katrusiak, 2017a) and abruptly at phase transitions (Andrzejewski & Katrusiak, 2017b). Another method of pressure calibration is based on the luminescence lifetime of lanthanide nanocrystals (Runowski *et al.*, 2017).

2.7.15. High-pressure diffraction data corrections

Apart from the Lorentz and polarization (Lp) corrections routinely applied to reflection intensities measured for bare crystals (*i.e.* crystals not enclosed in environment devices), as well as other corrections like extinction and absorption in the sample, the effects of the high-pressure cell should additionally be accounted for. These effects mainly include absorption in the pressure-vessel walls, shadowing of the sample by the pressure-cell opaque elements and elimination of the reflections of the diamond anvils for measurements in a DAC. The set of corrections is usually described for the specific pressure vessel. For a