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})
$Cr^{3+}:Al_2O_3$	$^2E\downarrow^4A_2$/d	6942	3.65 (9)	6.2 (3)	4.9	17.0
$Sm^{2+}:SrB_4O_7$	$^5D_0\downarrow^7F_0$/s	6854	2.55	−0.1	17.0	−0.4
$Sm^{2+}:BaFCl$	$^5D_0\downarrow^7F_0$/s	6876	11.0	−1.6	4.8	−1.5
$Sm^{2+}:SrFCl$	$^5D_0\downarrow^7F_0$/s	6903	11.2 (3)	−2.36 (3)	5.8	−2.1
$Eu^{3+}:LaOCl$	$^5D_0\downarrow^7F_0$/s	5787	2.5	−0.5	1.0	−2.0
$Eu^{3+}:YAG$	$^5D_0\downarrow^7F_1$/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 (l1)
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 $Sm^{2+}:SrB_4O_7$ (Lacam & Chateau, 1989; Lacam, 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

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

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 $\delta_{\alpha R} = \partial(\ln\alpha)/\partial(\ln V)_{TR}$. 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, CaF_2 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, 2017*a*) and abruptly at phase transitions (Andrzejewski & Katrusiak, 2017*b*). 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

typical DAC with the anvils (about 1.7 mm high) supported directly on the edges of conical steel or tungsten carbide windows, and for Mo *K* radiation, the absorption is quite uniform and varies between about 0.50 and 0.60, for the beams passing close to the DAC axis and those close to the conical window edge, respectively. This absorption is even smaller at the shorter wavelengths used for high-pressure X-ray diffraction studies at synchrotrons. For this reason the absorption correction for the DAC is often neglected.

The sample-shadowing correction accounts for the loss of intensity due to the sample being partly shadowed by the gasket edges. This effect can be avoided by choosing a sufficiently small crystal or by applying a sufficiently narrow beam, which would illuminate only the central part of the sample. Such microbeams are now routinely used at synchrotrons. For these reasons, synchrotron data are often used straightforwardly after applying just the Lp corrections and incident-beam variation and eliminating the diamond reflections. In fact there are very few diamond reflections because of the small unit cell and many systematic absences, and the DAC can be treated as a low-background cuvette for powder diffraction.

The corrections for absorption and gasket shadowing are very important for high-pressure data collection in the laboratory, where a sealed X-ray tube is used. Its beam is relatively weak and for this reason the quality of the data (signal-to-background ratio) is low, but can be improved by increasing the sample volume. Ideally, a sample that completely fills the DAC chamber secures the highest intensity of reflections. However, for large samples the shadowing of the incident and diffracted beams by the gasket is very significant and should be corrected for (Katrusiak, 2004*a*,*b*).

The calculation of the so-called analytical corrections, obtained by dividing the high-pressure chamber into small pixels and calculating the beam's trajectory to and off each pixel, through all the DAC components (beryllium discs, if present, diamond anvils, hydrostatic fluid and sample) can precisely eliminate errors. Having the correct reflection intensities simplifies the structure solution of new phases and increases the accuracy of the refined structure. It has been shown that some incompleteness of accurate data does not cause systematic errors in the structural parameters (Dziubek & Katrusiak, 2002). In most calculations of reflection intensity corrections, the cylindrical symmetry of the DAC about its axis is assumed (Katrusiak, 2001, 2004*a*,*b*; Hazen & Finger, 1982; Angel, 2004; Kuhs *et al.*, 1996; Miletich *et al.*, 2000).

Diffraction measurements with area detectors have the advantage of collecting data with a considerable redundancy factor, which is often routinely used to calculate the so-called empirical absorption corrections, which are sometimes applied to a sample in a DAC. The intensities of powder diffraction reflections measured at synchrotrons with microbeams are often not corrected, particularly when the DAC axis is not significantly moved from the primary beam during data collection. The redundancy of the data also considerably reduces the effect of simultaneous diffraction events by the sample and one or two of the diamond anvils.

The most significant systematic errors in the diffraction of a sample in a DAC may be due to preferential orientation of the grains, which can occur for an anisotropic sample and non-hydrostatic conditions in the chamber. This effect can be accounted for in the process of Rietveld refinement (McMahon, 2004; Filinchuk, 2010), or may require repetition of the measurement after reloading a new sample into the DAC.

2.7.16. Final remarks

During the last 100 years, and particularly during the last few decades, high-pressure diffractometric techniques have been developed covering a broad range of research in different fields of science. It is simply impossible to present all aspects of high-pressure methodology in one chapter. Many books, book chapters and scientific papers have been written on high-pressure research and therefore I have chosen to present a 'flavour' of high-pressure crystallography, rather than concentrating on all its aspects. Readers interested in specific subjects can find the required information in a number of instructive books (Hazen & Finger, 1982; Eremets, 1996; Holzapfel, 1997; Katrusiak & McMillan, 2004; Boldyreva & Dera, 2010; McMahon, 2012) and in numerous articles in research journals. This chapter is only an introduction and gives some useful reference information for high-pressure crystallographers.

It should be stressed that the sample-preparation techniques for high-pressure studies are relatively demanding. Therefore, diffraction studies are often 'adjusted' to the form of the sample obtained in the high-pressure device. In particular, powder diffraction, single-crystal and spectroscopic measurements can be conducted on some synchrotron beamlines (see *e.g.* Dera *et al.*, 2013). Many experimental techniques complementary to high-pressure crystallographic studies have not been mentioned here.

It can be concluded that, over the years, high-pressure research has become quite popular in materials science and at present all over the world there are hundreds or even thousands of scientists capable of performing high-pressure experiments. Their scientific output is significant, and can be used as a guide for those interested in specific types of high-pressure research.

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