On the temperature correction to the ruby pressure scale

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Since there is much confusion about the temperature correction to the ruby high-pressure scale, we have measured the temperature dependence of the ruby R1 and R2 lines for several ruby samples in the range 150–400 K. The results show a variation of 0.3 Å, corresponding to a pressure of 1 kbar. The results do not depend on chromium concentration. We find that the error in pressure can be reduced to about 0.4 kbar by measuring the temperature dependence of both the R1 and R2 lines of the ruby sample that are used in the high-pressure experiment.

The ruby fluorescence scale is a very useful secondary pressure scale in high-pressure science, because the pressure can be determined accurately and quickly by relatively simple means. One uses the redshift with pressure of the R1 and R2 fluorescence lines, which are emitted by Cr3+ ions in a sapphire Al2O3 lattice. The absolute accuracy of this scale is less than 2.5% up to 200 kbar, while the relative accuracy is much better, in the order of 0.1 kbar in our experiments. However, the ruby lines also shift with temperature. Correcting for this effect is important above 100 K, since a temperature change of 6 K has about the same result as a pressure change of 1 kbar. In the literature, different behavior of the R1 shift with temperature has been observed, although the origin of these differences is not clear. In Fig. 1, we have plotted the literature shifts with respect to a linear shift of 0.068 Å/K to increase the scale. It can be seen that at low temperature, the shifts have a variation of 1.1 Å and at high-temperature 2.4 Å corresponding to pressures of about 3 and 7 kbar. The difference in chromium concentration of the ruby samples cannot be a reason for the variations, since there is no systematic trend. On the other hand, it seems that most authors have performed a single measurement only and have not repeated the experiment. Since we found significant differences between our high-pressure results using the shift of Ref. 5 and data obtained by different high-pressure techniques, we decided to measure the temperature dependent shift of the ruby lines before and after each experiment.

The ruby used in our experiments is chipped from a single crystal, grown by Djeva. Electromicroprobe analysis of this crystal yields the following results for the composition: 0.61% (by weight) Cr3+, < 0.01% other ions. For comparison we have also performed experiments with one chip with a Cr3+ composition of 0.05% that originated from a laser rod. In all experiments, one or two chips of about 20 μm were contained in the closed gasket hole of our diamond anvil cell (DAC), that contained air at ambient pressure.

The ruby is excited with HeCd or Ar lasers, that are focused on the sample with an f = 200 mm lens. Since we once found a shift of 0.26 Å with 40 mW of Ar power, we always kept the laser power below a few mW to avoid heating of the ruby. With the HeCd laser, we did not observe heating at a power of 38 mW. The emitted fluorescence light is focused on the entrance slit of a Spektrohlab BM-100 1 m single monochromator, equipped with a photomultiplier and an absolute wavelength encoder. The slit-widths were 50 μm, corresponding to a spectral resolution of about 0.25 Å. The wavelengths were calibrated using the 6929- and 7032-Å emission lines of neon and the 6965-Å line of argon, by placing small emission lamps in front of the laser and omitting the DAC. We checked that variations of the room temperature of several K did not influence the monochromator calibration within 0.01 Å. The ruby spectra were measured over an interval of 22 Å with a stepsize of 0.1 Å and an integration time of 1 s by an Apple II microcomputer. The positions of the R1 and R2 peaks were obtained by fitting a parabola through 24 points around the maximum of the lines and taking the maximum of the parabola with a resolution of 0.01 Å.

The DAC is provided with a cold finger, projecting from a copper band around the DAC into a liquid N2 dewar. Resistive heaters are wound around the cold finger and the copper band and the whole system is contained in an insulating box. The temperature stability of this system is better than 0.1 K. The temperature is measured with a calibrated platinum resistance thermometer with an accuracy limited by gradients to ±0.5 K. The temperature dependence was measured every 15–30 K in the interval needed in the high-pressure experiments (usually 160–380 K). At each temperature, we waited about 5 min for equilibrium and then measured four spectra. The results of these four measurements were within 0.03 Å at low temperatures and 0.1 Å at high temperature. The ruby seemed to be in equilibrium, since no systematic drift with time was observed.

The resulting line shifts are fitted to quadratic or cubic polynomials, which have standard deviations of less than 0.1 Å. The results for ten samples of ruby (including the two curves from the 0.05% Cr3+ chip) are shown in Figs. 2 and 3, again with respect to a linear shift of 0.068 Å/K. The monochromator was calibrated on the same day each time an experiment was performed. It can be seen that at 160 K, the variation is 0.30 Å and at 380 K 0.27 Å, if the average of R1 and R2 is considered. The results of only R1
FIG. 1. Dependence of the ruby R1 line on temperature. A slope of 0.068 Å/K (Refs. 3 and 6) is subtracted and the shifts are with respect to 300 K. The full curve is of McCumber and Sturge (see Ref. 2), the long dashed curve below 300 K is of Buchsbaum et al. (see Ref. 8), the long dashed curve above 300 K is of Wunder and Schoen (see Ref. 7), the short dashed curve up to 380 K is of Diatschenko et al. (see Ref. 9), the dotted curve is of Adams et al. (see Ref. 4), the dash-dotted curve at low temperature is of Shchanov and Subbotin (see Ref. 5), the dash-dotted curve at high temperature is of Yen (see Ref. 12) and the dash-double dotted curve is of Munro et al. (see Ref. 10).

have a variation of 0.28 and 0.40 Å. The results for the 0.05% Cr³⁺ are indistinguishable from the others. We suggest for the temperature shift of the average of the ruby lines (R₁ + R₂)/2 in the temperature range 150-400 K:

\[
\Delta[(R₁ + R₂)/2](Å) = 6.554 \times 10^{-2}[T(K) - 300] + 8.670 \times 10^{-5}[T(K) - 300]^2 - 1.099 \times 10^{-7}[T(K) - 300]^3, \tag{1}
\]

and for R₁ only:

\[
\Delta R₁(Å) = 6.591 \times 10^{-2}[T(K) - 300] + 7.624 \times 10^{-5} \times [T(K) - 300]^2 - 1.733 \times 10^{-7}[T(K) - 300]^3. \tag{2}
\]

The results of 12 other experiments carried out with eight different ruby samples agree well with Eqs. (1) and (2). Since the monochromator was not calibrated on the day these experiments were carried out, they have not been taken into account in Eqs. (1) and (2). The variation is therefore slightly larger than in the experiments described above.

At temperatures below 300 K, our results are in agreement with those of Buchsbaum et al. and they are about the average of the literature shifts. Above 300 K, the results agree with those of Wunder and Schoen, Diatschenko et al. and Yen. Again, they are in the middle of the results from literature. The difference with the results of Munro et al. may be caused by their use of a sophisticated line-shape fitting procedure. On the other hand, one might expect their results to have a larger shift of the R₁ line; when the ruby lines overlap, the R₁ will undergo a smaller apparent shift with increasing temperature relative to the real shift which one would expect to obtain from curve fitting. Also, we expect this effect to become important only when the width of the R₂ line becomes as large as the separation between the two lines, which happens above 400 K. Differences with other authors may be easily explained by: heating in the laser beam, monochromator calibration errors, temperature gradients in the measuring cell, lack of thermal equilibrium, etc.

Since it has been suggested that the ruby may undergo irreversible changes at high pressures, we have compared the wavelengths and linewidths of the chips at ambient pressure before and after high-pressure experiments on condensed gases. No evidence for irreversible behavior was found over the full temperature range. Nevertheless, it is possible that this effect occurs at much higher pressures.
than reached in our experiments (about 100–200 kbar) or in nonhydrostatic pressure environments.

We measured the temperature dependence of the ruby lines in all our high-pressure experiments with the same sample of ruby before and after the experiment, under the same spectroscopic conditions. To cope with the line broadening of the lines with increasing temperature ($T>370$ K), the measuring interval was doubled by using a stepsize of 0.2 Å and at the highest temperatures ($T>450$ K), we used a stepsize of 0.4 Å with slitwidths of 100 μm. Furthermore, we used both R1 and R2 lines, which is not always recognized to be useful, although it is recommended in Refs. 1 and 4. With these procedures, it turns out that the reproducibility of different experimental runs is as good as about 0.4 kbar.

In summary, by using the temperature dependence of the ruby lines given in Eqs. (1) and (2) and measuring the fluorescent wavelength of the ruby sample at 300 K, the contribution of working at nonambient temperatures to the uncertainty in pressure is about 0.5 kbar. If higher accuracy is required, the temperature dependence of both R1 and R2 lines of the same ruby sample as used under pressure should be used. In our experience, the reproducibility is then about 0.4 kbar.

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