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Calibration of the Ruby Pressure Gauge to 800 kbar Under Quasi-Hydrostatic Conditions

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An improved calibration curve of the pressure shift of the ruby R_1 emission line was obtained under quasi-hydrostatic conditions in the diamond-window, high-pressure cell to 800 kbar. Argon was the pressure-transmitting medium. Metallic copper, as a standard, was studied in situ by X ray diffraction. The reference pressure was determined by calibration against known equations of state of the copper sample and by previously obtained data on silver.

INTRODUCTION

In recent years the ruby pressure gauge has been used as a secondary calibration standard for experiments that have extended to pressures as high as approximately 1 Mbar [*Mao et al.*, 1978]. Original calibration of the gauge involved observing the shift with pressure of the ruby R_1 luminescent line, and simultaneously, the specific volumes of several metals (Cu, Mo, Pd, and Ag) were measured by X ray diffraction. The absolute pressure was obtained indirectly by making reference to the isothermal equations of state of the metals derived from shock-wave data. Independent, although less accurate, primary calibration was determined by making precise measurements of force per unit area [*Mao et al.*, 1979]. The calibration measurements were carried out in a number of geometrical configurations of the metal calibrant samples to average the possible effects of nonhydrostatic stress.

The ruby gauge is normally considered as a working standard, and its calibration in rigid as well as quasihydrostatic pressure-transmitting media must be evaluated. In the present study the calibration experiments were done with argon as a pressure-transmitting medium. At pressures above approximately 12 kbar at 25°C argon becomes a weak solid, so the conditions of the calibration were quasihydrostatic. Measurements of the maximum pressure gradients in argon suggest that its shear strength is relatively low even at pressures of several hundred kilobars [*Bell and Mao*, 1981].

The purpose of the present study was to redetermine the calibration of the ruby gauge under conditions as close as possible to those of a fluid pressure environment at 25°C. Data on metallic copper obtained in the present study were used with data on metallic silver of *Zou et al.* [1982] for the calibration. As in the previous calibration under nonhydrostatic conditions, the unit cell volumes of metals were measured for calibration of pressure with reference to known equations of state. A discussion of analysis of the shock Hugoniots of copper and silver used in the present study is given by *Mao et al.* [1978].

EXPERIMENTAL METHOD

The diamond window, high-pressure cells employed in these experiments are of the MBC-Y(L2) design described by *Mao and Bell* [1978]. Powdered samples of copper and ruby were introduced into the sample chamber of a preindented gasket. The cell then was set in a special high-pressure cylinder similar in design to apparatus developed by *Mills et al.* [1980] at the Los Alamos National Laboratory. With the cell in place, dense fluid argon was pumped into the cylinder, filling all the volume including the sample chamber at a pressure of approximately 2 kbar. The cell was sealed and the sample chamber pressure raised to approximately 10 kbar by means of an external, remote, automated system. The cell was removed from the cylinder for study by X ray diffraction and by laser-induced fluorescence spectroscopy techniques [*Bell and Mao*, 1975].

X ray diffraction measurements were made by placing the high-pressure cell in an X ray beam produced in a Rigaku, rotating-anode generator. The cell was held in a centerable cradle and was aligned to an 80-μm-diameter X ray collimator. The sample was approximately 6 μm thick; the path length through the argon pressure-transmitting medium was approximately 20 μm. The ratio of sample volume to the volume of argon was approximately 1 : 5. The sample chamber was 150 μm in diameter, so it was necessary to position the collimated beam accurately to within 5 μm of the center. Debye-Scherrer diffraction lines were recorded by two methods, one with a standard film cassette of 50 mm radius, and the other with a new adaptation of the curved, position-sensitive, flow-proportional detector (CPSD) [*Xu et al.*, 1984] manufactured by the M. Braun Company (model OED50). The Cu (111) X ray diffraction line was observed with the CPSD, and the Cu (200) line was observed by film.

Gas pressure in the detector was held at 12 bars above ambient. The gas composition was xenon 89.7%, methane 10.3% by volume. A flow rate of 1 cm^3/min was established. The detector sampled 10° of arc at a radius of 200 mm. Multichannel analysis and digital count storage had a density of 800 channels, which corresponds to an absolute resolution of 50 μm along the arc. This resolution is equivalent to that obtained in film measurement. Exposure time with the CPSD is considerably shorter, by a factor of 3, resulting in less instrument drift and significantly better intrinsic resolution of the X ray diffration lines. The reason both film and CPSD methods were employed in this study was that in some instances irregular X ray lines due to large grain growth of argon required the use of film. The film cassette has a wider arc (80°). These materials had not previously been studied extensively at pressures this high, and although, as it turned out, no new phases were detected in this study, it was considered prudent to explore a broad region in 2Θ space. Calibration of the CPSD was done by the methods developed by

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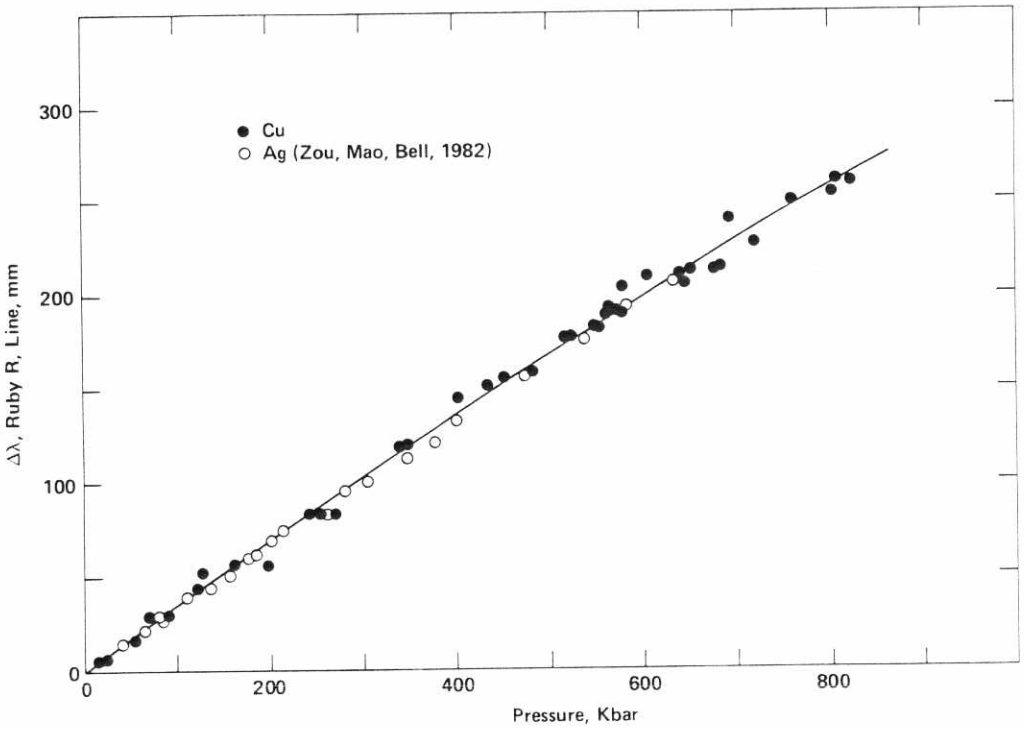

Fig. 1. Calibration curve of the shift with pressure of the wavelength of the ruby R_1 luminescent line. Solid circles, copper standard; open circles, silver; argon pressure-transmitting medium.

Mao et al. [1983]. A discussion of the accuracy and uncertainties is given in the same paper. Calibration of the sample to film or detector distance was done by the use of an external sample of tantalum on one of the large diamond table faces.

RESULTS

Figure 1 shows a plot of the shift in wavelength of the ruby R_1 emission line versus pressure. Solid circles are calibration points for the specific volume of copper (this study); open circles are for silver [after *Zou et al.*, 1982]. As described above, the copper calibration points were obtained in this study by determining the unit cell volume by X ray diffraction, and then, by making reference to the shock wave equation of state, the corresponding value of pressure [*Mao et al.*, 1978] was obtained. Values of the specific volume of silver were obtained from the previous results of *Zou et al.* [1982]. The data are listed in Table 1. At each step where the pressure was measured by the equation-of-state determinations, the ruby R_1 line shift was also measured, thus yielding a pressure calibration of the shift.

Scatter of the values was generally less than 5% of the pressure. Departure from a linear function was a result of the gentle curvature of the R_1 shift versus pressure relation. Individual scatter beyond that inherited from the shock wave data appeared to result mostly from the character of the argon pressure medium. Argon is quasi-hydrostatic, but nonetheless solid argon supports a small but finite pressure gradient across the sample chamber. The maximum gradient observed in the study was 17 kbar (at 700–800 kbar, Figure 2). Additionally, there could have been grain contact effects that resulted in local stress deviations apart from effects of the pressure-transmitting medium. Random errors in the shock wave experiments are of the same magnitude as that of the observed scatter, a result suggesting that it may be impossible to reduce the uncertainty. The errors introduced by data reduction of the copper and silver Hugoniots, however, were negligible, as discussed by *Mao et al.* [1978]. Thus only experimental precision is significant in the calibration.

The calibration curve in Figure 1 was fitted to the copper volume versus pressure determinations as follows. The initial slope was taken from the ruby line-shift calibration of *Piermarini et al.* [1975]. The curve was then derived from a nonlinear least squares fit to the copper and silver points. The resulting relation is as follows:

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

where P is the pressure in megabars, λ is the wavelength of the ruby R line, $A = 19.04$ Mbar (the initial slope [after *Piermarini et al.*, 1975]), $B = 7.665$. This calibration relation yields higher pressures per shift of the ruby R_1 line than the previous calibration that was measured under nonhydrostatic conditions, a result suggesting that the previous calibration was conservative [*Mao et al.*, 1978].

DISCUSSION OF THE RUBY PRESSURE GAUGE

Recalibration of the ruby pressure gauge in this study suggests that pressures measured by the original calibration [*Mao et al.*, 1978] were slightly low at the high-pressure end of the scale. Nonetheless, the new calibration function falls within the uncertainty limits (±6%) of the older calibration.

Deviations that result from nonhydrostatic stress are two fold. One effect results from the uniaxial nature of the loading

TABLE 1. Compressibility Data for Cu and Ag

Cu[a]		Ag[b]	
P,[c] kbar	$\Delta\lambda$,[d] Å	P,[c] kbar	$\Delta\lambda$,[d] Å
14.4	6.3	41.0	14.5
24.8	6.3	65.0	22.0
53.7	16.7	80.0	28.5
70.2	30.5	83.0	27.5
70.2	35.5	110.0	40.0
121.1	43.3	135.0	44.0
128.8	52.4	155.0	51.5
160.2	56.0	176.0	60.5
198.4	56.6	182.0	62.0
241.0	88.1	200.0	68.5
255.7	88.4	213.0	75.0
264.7	88.1	260.0	83.0
340.0	119.5	280.0	97.0
346.0	119.5	304.0	101.0
403.8	144.2	347.0	113.0
434.0	152.8	378.0	122.0
453.3	155.6	400.0	133.0
482.8	158.7	474.0	157.0
517.2	176.3	538.0	176.0
522.8	176.5	584.0	193.0
547.1	182.8		
551.3	182.2	634.0	207.0
562.1	188.9		
570.4	191.8		
577.1	188.9		
564.7	193.1		
580.3	202.7		
646.0	207.1		
605.3	209.2		
641.4	209.6		
650.6	212.5		
677.9	212.5		
679.1	212.5		
720.6	228.3		
692.9	239.8		
762.3	249.0		
804.3	254.1		
823.2	259.3		
809.1	260.2		

[a]This study.
[b]After *Zou et al.* [1982].
[c]Pressure determined from volume equation of state, see text.
[d]Shift of the ruby R_1 line.

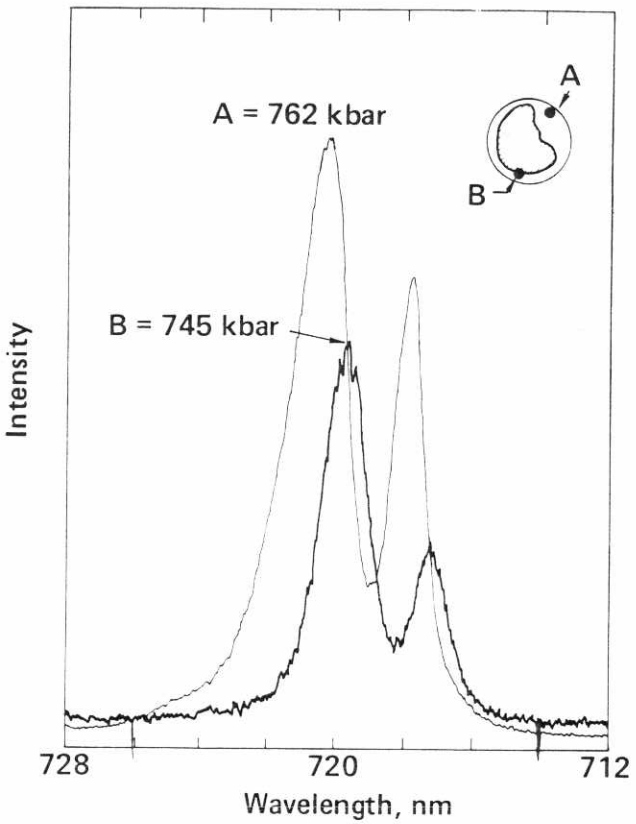

Fig. 2. *R* line luminescent spectra of ruby crystals at 750 kbar nominal pressure. Inset is sketch of the sample chamber of the diamond-window, high-pressure cell containing (A) argon (clear) and (B) sample of powdered copper (hatched) and ruby (solid circle).

force in the diamond window, high-pressure cell in combination with the geometric aperture of the diffracted X ray beam in measurements of unit cell volume. This effect has been demonstrated to be minor [*Mao et al.*, 1978]. Nonhydrostatic stress applied to the ruby crystals being observed could also have an effect. Figure 2 shows *R* line luminescent spectra of ruby grains totally immersed in argon (A) and on the edge of the metal sample (B). At each pressure the ruby emission was measured at 10-12 points within the sample chamber. The pressure difference of 17 kbar at approximately 750 kbar is not unusual (2% of the pressure). That the two spectra are well resolved indicates little or no observable line broadening. The pressure gradient is gradual across the sample chamber, a result reflecting the apparent strength of solid argon.

This new quasi-hydrostatic pressure calibration system is designed for experiments in the diamond window, high-pressure cell at room temperature (25°C). The argon pressure-transmitting medium has the advantage of providing quasi-hydrostatic stress on a sample under study as well as on ruby grains placed in the sample chamber. Spectroscopic data obtained with the argon medium are well resolved and, therefore, superior to those obtained in the past with rigid solid media. Luminescence observations of the ruby *R* lines are well resolved, and thus the ruby pressure scale is precise and reproducible within the limits imposed by pressure gradients.

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