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Calibration of the pressure dependence of the R_1 ruby fluorescence line to 195 kbar

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The pressure dependence of the R_1 ruby fluorescence line has been calibrated at 25 °C against the compression of NaCl. Pressures are determined using the Decker equation of state for NaCl. The dependence is linear to 195 kbar following the equation $P_{\mathrm{NaCl}}=2.746(\Delta\lambda)$, where P is in kbar and $\Delta\lambda$ in Å. The uncertainty in the value of the slope, $dp/d\lambda$, expressed in terms of a 95% confidence interval is 2.746 ± 0.014 kbar Å^{-1}. The coefficient of the quadratic term $(\Delta\lambda)^2$ is not significantly different from zero; and the quadratic term makes indeed a negligible contribution to the fit. Taking into account the reported uncertainty associated with the Decker equation of state for NaCl, the value of the slope is 2.740 ± 0.016 kbar Å^{-1} within a 95% confidence interval.

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INTRODUCTION

Recently, a preliminary report describing a new pressure measurement technique which utilizes the pressure-dependent spectral shift of the sharp ruby (α-$Al_2O_3:Cr^{3+}$) fluorescence R lines was published from this laboratory.[1] In that report it was demonstrated that a small fragment of ruby as small as 1% of the total pressurized sample volume could serve as a continuous pressure sensor when placed in a gasketed diamond-anvil-type optical pressure cell. Fluorescent R-line emission from the small fragment of ruby excited by high-intensity incident light can be analyzed for wavelength displacement due to a pressure effect. The approximate pressure dependence of the R_1 line was determined from preliminary measurements using known freezing pressures of several liquids chemically inert to ruby. The results of those measurements indicated an approximately linear pressure dependence (-0.77 ± 0.03 cm^{-1}/kbar or 2.7 ± 0.1 kbar Å^{-1}) up to about 23 kbar. In those experiments the diamond-anvil pressure cell was used with metal gaskets to contain the ruby sample and the liquid pressure transmitting medium, but it was noted also that the method is applicable to any pressure system with optical access.

Later, a description of an optical system for rapid routine quantitative pressure measurement in the diamond-anvil cell using the new fluorescence technique was published.[2] This system was used to evaluate the merits of several fluorescent materials, including ruby, as continuous pressure sensors as described in that report. The results of that study showed that, in general, ruby is superior to all the other materials studied according to the criteria established for selecting an optimum pressure sensor.

Using ruby as the pressure sensor, the optical system for pressure measurement was used to characterize the hydrostatic properties of several solids and liquids commonly used as pressure transmitting media.[3] In that study it was established that, in addition to the ruby R_1 line shift, line shape also provides critical information concerning the hydrostatic nature of pressures produced in solids and liquids as suggested earlier.[1] Also in that work, the hydrostatic limit was extended from the previously accepted value of 65 kbar produced by a 1:1 mixture of pentane-isopentane with the discovery that a 4:1 mixture (by volume) of methanol:ethanol produces a hydrostatic environment to over 100 kbar. The ruby pressure measurement method has now become routine and several results using the technique have been published.[4-6] Since the method is rapidly being adopted in other high-pressure laboratories, the need for a definitive calibration is apparent.

Here, we report details describing the calibration of the pressure dependence of the sharp fluorescence R_1 line in 0.5% Cr-doped ruby at 6942.4 Å at 25 °C. The wavelength shift was calibrated against the compression of NaCl at 25 °C. Pressures were derived from the Decker equation of state for NaCl which is reported to give pressures accurate to 3% at 300 kbar.[7] Several independent checks are available to verify and substantiate the validity of the pressures predicted by the Decker equation of state for NaCl. For example, (a) the agreement with the pressures assigned to the Ba I-II and the Bi III-V fixed-point transitions at 55 and 76 kbar, respectively, as determined using a piston-cylinder apparatus in a calibration experiment, are within the uncertainties reported for the theory[8,9]; (b) pressures calculated from the equations of finite strain using MgO (which is very incompressible and thus useful in this context) agree to 300 kbar within 3% with the theory,[10,11] and the pressure-volume relationship obtained from shock measurements on NaCl agree to within 2% at pressures to 300 kbar.[11] The uncertainty in the theoretical calculation, which is due to experimental error in the input parameters, as well as any approximation inherent in the theory, is presently of the same order of magnitude as the attainable accuracy for measured pressures using x-ray techniques. Thus, there is no way at present to improve on current theory by experimental measurement. In the absence of a better primary pressure standard above 50 kbar, we have chosen the Decker equation to calibrate the pressure dependence of the ruby R_1 line.

EXPERIMENTAL PROCEDURES

The procedure for determining the compression of NaCl consisted of an x-ray powder diffraction experiment in which the lattice constant of the cubic material was determined at various pressures up to a maximum of 195 kbar. To obtain this information a specially designed camera with a flat-plate film cassette positioned 12 cm from the sample was constructed for recording the x-ray powder pattern in the forward reflection mode. A Waspaloy-type diamond-anvil pressure cell similar to one previously described[2] was employed with the sample in a gasketed configuration.

The gasketed sample consisted of finely powdered ACS grade NaCl (99.98% purity) and finely powdered ruby (0.5% Cr). The ruby powder was prepared by crushing single-crystal Verneuil-grown chips. Both materials were passed through a No. 325 mesh sieve before being intimately and thoroughly mechanically mixed in the proportions of 4 parts NaCl and 1 part ruby by volume. An Inconel X750 gasket approximately 0.15 mm in thickness and containing a hole 0.3 mm in diam was loaded with enough of the NaCl-ruby mixture to occupy half the volume defined by the gasket hole dimensions. The gasket hole was then completely filled with a 4 : 1 methanol : ethanol mixture before sealing with the diamond anvils. It should be pointed out, however, that sample composition can only be approximated because some material may be lost as effluent as the gasket is sealed and deformed by the two diamond anvils when the load is applied. The amount of sample loss is unpredictable and is specific for each experiment. In this particular case, there appeared to be little sample loss, if any, and that which may have occurred consisted mainly of the methanol : ethanol mixture. Because techniques for loading gaskets in diamond-anvil pressure cells have been described extensively[12,13] no details are given here.

The measurement procedure consisted of obtaining both x-ray data on NaCl and wavelength data on the ruby R_1 line first with maximum load on the diamond cell, and then successively reducing load in increments equivalent to 10—20 kbar, and recording data at each of these intervals until the final measurement was made at 1 bar.

In general, three consecutive measurements were made after each major load reduction. A period of at least 5 h was observed after each load reduction before initiating the ruby and x-ray measurements. The R_1 line shift was determined before and after each x-ray pattern was obtained using our recently developed optical fluorescent system.[2]

The Waspaloy pressure cell was designed with an exit aperture which allowed a maximum 2θ value of 26° to be recorded on film. Typical exposure times of 15 h using Zr-filtered MoK_α radiation were required.

Two independent sets of data were obtained. One set included measurements in a purely hydrostatic pressure environment and extended over the range from 1 to about 104 kbar. The other set of measurements were made to 195 kbar with the data up to 104 kbar obtained in a hydrostatic environment and from 104 to 195 kbar in a quasihydrostatic state.

RESULTS

Because the measurements were made in two different kinds of pressurized environments, i.e., hydrostatic and nonhydrostatic, it was considered necessary to treat the data for three types of cases to determine if significant differences existed among them. Case (1) consists of data obtained for the completely hydrostatic condition; case (2) is made up of data from the quasihydrostatic environment only, i.e., between 104 and 195 kbar; and case (3) includes the combined sets of data from 1 bar to 195 kbar.

Two least-squares fits were made. In the first, both a linear equation, $P_{\mathrm{NaCl}} = A(\Delta\lambda)$, and a quadratic equation, $P_{\mathrm{NaCl}} = A(\Delta\lambda) + B(\Delta\lambda)^2$, were fitted to the pressure P (determined by using Decker's equation of state and our NaCl compression data) and the wavelength shift, $\Delta\lambda$, for the ruby R_1 line. Since the errors associated with the x-ray measurement are two to five times larger than the error associated with the $\Delta\lambda$ measurement, each data point was weighted according to the uncertainty associated with the x-ray measurement only (0.10% in lattice parameter determination). The results of this procedure are listed in Table I for the three unprimed cases mentioned. The values and uncertainties associated with the parameter, B, indicate, in each case, that the curve is essentially linear. Furthermore, the values of the slope, A, for each case, overlap with each other within a 95% confidence interval and indicate that there is no reason to segregate the data with respect to the nature of the pressure environment. As a consequence, the calibration is based on all of the data points, i.e., case (3).

The combined errors in the $\Delta\lambda$ and P measurements are reflected in the spread of the points about the fitted line as shown in Fig. 1 for case (3). This term can be expressed as the standard error of estimate or the standard deviation of the points about the fitted line and is shown for each case under the column heading, S, in Table I. The standard error of the estimated slope for case (3) is 0.007 for the 47 points, and the 95% confidence interval for the slope, $dp/d\lambda$ is 2.746 ± 0.014 kbar/Å.

A second series of least-squares fits was made using

TABLE I. Results of least-squares fit to pressure vs ruby R_1 fluorescence line data.

Case	Set[a]	N[b]	Slope[c] (A) (kbar/Å)	Quadratic Coeff.[d] (B)	S[e] (kbar)
(1)	$P<104$	28	2.735 ± 0.030	0.003 ± 0.003	1.4
(2)	$P>104$	19	2.753 ± 0.012	−0.0002 ± 0.0014	0.7
(3)	$P<195$	47	2.746 ± 0.014	0.0006 ± 0.0006	1.2
(1′)[f]	$P<104$	28	2.728 ± 0.030	0.003 ± 0.003	1.3
(2′)	$P>104$	19	2.753 ± 0.012	0.0002 ± 0.0014	0.4
(3′)	$P<195$	47	2.740 ± 0.016	0.0009 ± 0.0008	1.0

[a] Pressure range, P, in kbar.

[b] N is the number of data points.

[c] Slope $(A) = dp/d\lambda$ in fit $P = A(\Delta\lambda)$; the ± interval represents a 95% confidence interval for the coefficient A.

[d] Value of B in fit $P = A(\Delta\lambda) + B(\Delta\lambda)^2$; the ± interval represents a 95% confidence interval for the coefficient B.

[e] S is the standard error of estimate or standard deviation of the points about the fitted line for $P = A(\Delta\lambda)$.

[f] Primed cases include total uncertainty in the weighting scheme. Unprimed cases contain only the uncertainty due to the x-ray measurement.

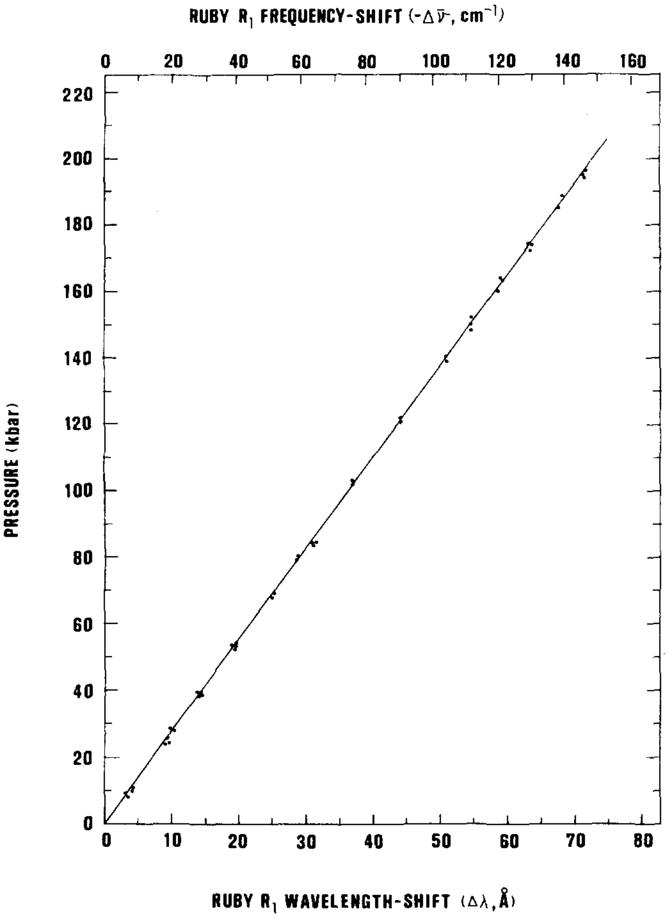

FIG. 1. The pressure dependence at 25 °C of the ruby R_1 fluorescence line at 6942 Å as a function of wavelength (Å) and also wave number or frequency (cm^{-1}). Pressure values are based on the Decker equation of state for NaCl.

the equations $P=A(\Delta\lambda)$ and $P=A(\Delta\lambda)+B(\Delta\lambda)^2$ and a weighting scheme which takes into account the estimated uncertainties in the pressure values derived from the equation of state as well as the uncertainties from the x-ray measurements. The reported values for the uncertainty in the Decker equation are ±1.1% below 50 kbar, ±1.7% below 100 kbar, and ±2.4% below 200 kbar.[7] In these fits each point in the least-squares fit was weighted in terms of the total uncertainty involved in determining each value associated with the point. The uncertainty involved in determining the pressure value arises from two sources: (a) the x-ray measurement and (b) the uncertainty in the input parameters, but not including any approximation inherent in the theory in Decker's equation. The uncertainty in the x-ray measurement is approximately 1 kbar at low pressures and increases to about 3 kbar at the higher pressures. The reported uncertainty in the Decker equation approaches zero at low pressures and increases to approximately 5 kbar at 200 kbar. Thus, the total uncertainty in P which should be used to determine the weights for the least-squares fitting varies from about 1 kbar at 10 kbar to about 8 kbar at 200 kbar. The estimate of 1 and 3 kbar for the uncertainties in the x-ray measurements is based on an approximate uncertainty of 0.10% in the lattice parameter determination. Expressing the uncertainty, as before, in terms of 95% confidence intervals, the weighted least-squares fit gives the results listed in Table I for the three primed cases. From these results it is clear that we can fit our data to pressures as predicted by Decker's equation of state with the equation for case (3):

$$P=2.740(\Delta\lambda).$$

The 95% confidence interval for the value of the slope, $dp/d\lambda$, is 2.740 ± 0.016 kbar/Å. This is the equation we recommend for determining pressure by the ruby R_1 line shift. However, it must be pointed out that, although statistics indicate that the slope is well characterized, in terms of precision, it is misleading to conclude that absolute pressures can be determined within the same error limits. We note that the overriding uncertainty is in the Decker equation, and suggest that the error limits in absolute pressure as determined by the ruby method reflect this uncertainty.

It is important to realize that the determination of the slope, $dp/d\lambda$, as determined here applies to pressures defined by Decker's equation of state for NaCl. There is nothing in our procedures which can allow us to relate to pressures on an absolute scale. Furthermore, any uncertainty in Decker's theory is a systematic uncertainty as it relates to our work and cannot be treated as a random error.

The pressure dependence of the R_1 line wavelength displacement is linear to within the accuracy of our measurements. The change in wavelength at the maximum of 200 kbar is 1%, not a very large effect, and from this point of view is compatible with a linear dependence. Departure from linearity should eventually take place, but the pressure necessary to effect this may be considerably greater than 200 kbar. Thus, the useful range of ruby as a pressure sensor may extend over a significantly greater pressure range than 200 kbar, and its potential will be explored further. The linear feature of the calibration relative to the equation of state of Decker, which in itself exhibits a very large curvature over the pressure range studied, suggests that the form of Decker's equation (and thus to some extent the reliability at the higher pressures) is perhaps better than would have been anticipated.

It is of interest to determine the pressure dependence of the R_1 line with respect to frequency or energy. In keeping with the commonly accepted practice in this field, optical frequency (or energy) is expressed in wave-number (cm^{-1}) equivalents. A least-squares fit of P(kbar) vs $\Delta\bar{\nu}$(cm^{-1}) weighted as outlined for the second procedure above shows in Fig. 1 a linear dependence with a negligible high-order term for case (3′):

$$P_{\mathrm{NaCl}}=-1.328(\Delta\bar{\nu})+0.0003(\Delta\bar{\nu})^2.$$

It is impossible to have the P-vs-$\Delta\lambda$ and the P-vs-$\Delta\bar{\nu}$ relations both linear with no quadratic term. Because $\bar{\nu}=1/\lambda$, if P vs $\Delta\lambda$ is taken as linear, then the P-vs-$\Delta\bar{\nu}$ relation must show a second-order term that contributes about 0.5% at 200 kbar in the expression

$$P=A(\Delta\bar{\nu})+B(\Delta\bar{\nu})^2.$$

However, with the uncertainties given for the A values (±0.008), the small B term becomes undetectable and nonlinearity is masked because of the magnitude of the errors involved. The standard deviation for the B term is ± 0.0002, almost equal to the value of B itself. The Student's t test for the quadratic term indicates, however, that nonlinearity is at the threshold of significance.

From reported shock data on Al_2O_3, a linear approximation to the Hugoniot in the range 1 bar to 200 kbar can be made.[14] Although there is curvature in the Hugoniot over the entire 1400-kbar range considered, in small (200 kbar) increments, a linear approximation is quite reasonable. In the interval 1–200 kbar, a linear approximation to the slope, dv/dp, gives -0.00026 cm^3/kbar for pure Al_2O_3 single crystal. Assuming that the mechanical properties of the 0.5% Cr-doped Al_2O_3 single crystal are similar to the pure material, then a relationship between $\Delta\bar{\nu}$ (cm^{-1}) and v (cm^3/g), the specific volume at pressure, can be derived, if the temperature effect in the Hugoniot is neglected. The frequency vs specific volume dependence must be linear in the pressure range measured because dv/dp is assumed constant and $d\bar{\nu}/dp$ from our data is also constant. Thus, $d\bar{\nu}/dv = 2.9\times10^3$ cm^{-4}.

DISCUSSION OF ERRORS

In the experimental procedures described herein, the sources of error are numerous, and in some instances extremely difficult to identify and analyze. The more significant ones are as follows:

(1) The small number of diffraction rings measured and used to calculate the NaCl lattice parameter;

(2) the error in the diffraction-ring diameter measurement which is related to the camera distance (sample-to-film distance);

(3) the dimensional change in photographic film due to processing and temperature effects;

(4) the pressure distribution or nonhydrostaticity in the NaCl-ruby-methanol : ethanol sample;

(5) the change in sample-to-film distance as a result of variable high loads on the anvil assembly;

(6) pressure intensification due to mixtures of materials of widely different mechanical properties in the pressurized sample volume;

(7) pressure instability in a gasketed sample over a duration of time;

(8) the theoretical uncertainty in the equation of state for NaCl;

(9) error in the wavelength measurement of the R_1 ruby fluorescence line.

The first seven of these factors play an important role in affecting the accuracy of the NaCl compression measurement. Because of their importance, each is discussed and evaluated separately. A potential major source of error is in the x-ray diffraction measurement from which the compression of NaCl is determined and then used to obtain a pressure through the Decker equation of state. Obviously the accuracy of the pressure value depends on the accuracy of the compression measurement excluding the inherent error in the equation of state. It is also clear that the more diffraction lines one observes and uses in the determination of the compression the more accurate that value will be.

The Waspaloy cell was designed with an effective 2θ aperture of about 26° and allows five diffraction rings of NaCl, the 111, 200, 220, 311, and 222, to be recorded on film using MoK_α radiation. This aperture was optimized to allow a maximum diffraction angle consistent with the magnitudes of the applied loads required to produce pressures up to 200 kbar on gasketed samples without diamond failure.

Although five diffraction rings should be available, two relatively weak lines, the 311 and the 222, were not measurable because of high background levels probably due to incoherent scattering from the diamonds. In most instances the 111 line was obscured by an unusually high background halo which covered a 2θ range from 8° to 14° and persisted throughout the entire set of experiments. This halo is attributed to incoherent scattering of the diamonds. At moderate and high pressures the 220 ring became obscured by overlapping with an Inconel diffraction ring which had become unusually broadened because of large pressure gradients within the gasket and unfortunately could not be measured. However, at all the pressure points studied the 200 line was clearly visible, well defined, and very sharp. The compression measurements are primarily based on the 200 diffraction ring, since the difficulties mentioned above could not be eliminated by a suitable gasket substitute at this time. Probably improved collimation by reducing the beam diameter to much less than the gasket diameter would improve the NaCl diffraction pattern. However, this would extend the exposure times (currently 15 h) required excessively, and it was decided not to pursue this approach at this time. In principle, the relative volume of a cubic material such as NaCl can be calculated from the position of a single diffraction ring. This is particularly true when the sample is in a completely stress-free or near-stress-free state so that strain and preferred orientation are essentially eliminated. We think that substantially this situation applies to these experiments.

In our diffraction arrangement the gasketed sample (approximately 0.3 mm in diam) contains powdered NaCl, powdered ruby, and a methanol-ethanol mixture, and is pressurized between two opposed diamond anvils. The x-ray beam passes through the gasket hole, which acts also an additional collimator, perpendicular to the anvil faces and produces a transmission-type diffraction pattern of rings on a flat-plate film cassette 12 cm away. The large sample-to-film distance was used to minimize reading errors in the ring diameters. In general, a standard deviation of ±0.08% was obtained for the precision of the 200 d-spacing measurement. This standard deviation is based on as many as 18 measurements of the diameter of the 200 diffraction ring in equally spaced azimuths.

A correction taking into account permanent dimensional changes in the 5-in. × 7-in. film due to photographic processing and possibly temperature effects was applied to the film measurements. The corrections were determined by measuring the linear distances among four fiducial marks located near the corners of the rectangularly shaped film. The standard deviation in the correction values were on the average about one-half the magnitude of the standard deviation in the diameter measurement of the 200 diffraction ring.

Another factor which affects the accuracy of the compression measurement is the presence of pressure gradients in the NaCl sample. Pressure gradients produce strain and preferred orientation in the sample as well as a pressure distribution. Obviously, the greater this distribution, the poorer the quality of the diffraction pattern particularly with respect to line broadening and intensity changes. When such a condition applies, an average compression may be determined by measuring the position of the middle of the broadened line.

In our experiment the pressure distribution was minimized by using a gasketed sample with a methanol-ethanol mixture as the pressure transmitting medium. This mixture was shown to produce a hydrostatic environment to about 104 kbar.[3] Thus our compression measurements below this pressure are for a truly hydrostatic environment. The typically sharp and well-defined appearance of the NaCl diffraction patterns obtained for this pressure range support this contention.

Above 104 kbar a quasihydrostatic state does exist in the NaCl sample. However, our ruby line-broadening measurements show that at 195 kbar the maximum pressure gradient in the NaCl sample is on the order of 14 kbar or about 7% of the average pressure value. At this level of stress, line broadening of the NaCl diffraction patterns was not significant and its effect was minimized by reading the line position at its center. Nevertheless, two calibration determinations were made, one for the hydrostatic range, and the other for both the hydrostatic and quasihydrostatic ranges to 195 kbar to verify this.

Also affecting the accuracy of the compression data is the change in sample-to-film distance which may occur as a result of the large loads applied to the anvils. Whether or not this effect is significant depends on the design of the cell as well as the procedures followed during the course of the experiment.

With regard to design, it is important that elastic or permanent distortion or bending in components of the cell as a result of large applied loads do not occur. Diamond-anvil indentation in the metal support behind the anvils is also a factor to be considered as well as elastic deformation in the anvils themselves. We have essentially eliminated the anvil indentation by employing hardened high-strength-steel anvil supports with relatively large bearing surface areas.

Our procedures consisted of initiating the compression measurements with the maximum load on the anvils. This ensured that the gasket was permanently deformed in thickness, diameter, and shape to its maximum extent. Because all subsequent measurements of a series were made at lower applied loads, no further gasket deformation is produced and thus no change in sample position in the cell due to this effect is expected during the course of the experiment.

We did observe, however, an elastic bending of the cell body which affected the sample position. The extent of bending of the cell body was accurately measured using a sensitive micrometer, and the sample displacement, which amounted to a maximum of 0.3 mm at 195 kbar, was calculated from the geometry and dimensions of the pressure cell. The effect was significant and corrections to the sample-to-film distance were applied.

Another factor affecting the accuracy of the compression measurement is the complex stress configuration which develops in mixtures of materials of dissimilar mechanical properties, primarily compressibility. The problem of stress differences in materials due to encapsulation has been treated in detail[15] and pressure differences in materials due to flow and geometry have also been described.[16] Experimental evidence for pressure differences in dissimilar materials in intimate contact has also been reported for two different mixtures of Nb and NaCl.[17] The effect was shown to produce a higher pressure on the less compressible Nb relative to the pressure on NaCl in a 19% Nb-81% NaCl mixture.

In our system the problem is even more complex since our sample contains three components, 10% ruby, 40% NaCl, and a 50% methanol-ethanol mixture. As long as the pressure on the system is below the hydrostatic limit no problem arises. However, when the hydrostatic limit has been exceeded and the fluid mixture becomes a glass, the particles of the various materials are not necessarily in the same pressure environment. The ruby, being the most incompressible component, should experience a higher pressure than either the NaCl or the glassy phase according to this theory, and hence would produce a greater fluorescence shift than expected. However, if one realizes that the ratio of compressibilities of ruby and NaCl at 200 kbar is only 2.5 compared to a ratio of 16 at atmospheric pressure and that pressures in our system are completely equalized at 104 kbar, the effect under consideration will be greatly reduced. The fact that no difference in the slope $dp/d\lambda$ above and below the hydrostatic limit was detected implies that the effect is within the established limits of our measurements, and thus we neglect it.

There is no doubt that a relaxation time is required on the order of 5 h immediately following a load reduction in the diamond cell before equilibrium pressure is reached. This has been demonstrated in an earlier report[3] for various materials both solid and glasses for which pressure drops were noted in samples over a period of 16 h duration. However, we have now established that most of this relaxation occurs within the first 5 h following a load change. For this reason, measurements were made after a waiting period of at least 5 h was observed following a major load reduction. No significant changes in pressure were observed after this period.

An uncertainty for which at present no correction can be applied is the inadequacy in the theory describing the behavior of NaCl under pressure. We thus take as our estimate of error associated with the x-ray measurement a combination of the film reading uncertainty of 0.08% and an uncertainty in film to sample distance of 0.06%. These uncertainties are combined as random errors and the rms value of 0.10% yields an uncertainty in the lattice parameter of NaCl which in turn determines the uncertainties in pressure (for example, 4.8% at 20 kbar, 2.1% at 100 kbar, and 1.8% at 200 kbar). The values obtained in this way provided the weighting factors used in the first least-squares procedure. These uncertainties were combined in a similar manner to the uncertainties associated with the theory to obtain weights for the second least-squares procedure.

Finally, the accuracy of the calibration curve is influenced by the error in the wavelength measurement. We had reported earlier that our optical system[2] was capable of an ultimate precision of 0.18 Å in our wavelength measurement. To achieve this required temperature control to ± 1 K and also required minimizing aberration effects due to excessive deviation from the optic axis of the system.

To check our wavelength measurements we used a $\frac{3}{4}$-m Spex monochromator and duplicated the measurements for one entire set of data. The agreement was within 0.2 Å which we estimate is our uncertainty in the wavelength measurement. This uncertainty is a constant and applies over the entire 195-kbar pressure range. Compared with the uncertainty in the pressure values, the error in the λ measurement is always less than the uncertainty in the pressure associated with the x-ray measurement, and at pressures above 50 kbar the uncertainties in pressure associated with the theory is comparable with the error associated with the x-ray measurement. It is apparent that neither the x-ray measurement nor the ruby technique is suitable for measurements at low pressures, i.e., below 10 kbar, with any degree of accuracy because of their low sensitivity. At higher pressures the ruby method becomes increasingly more significant, particularly above 50 kbar, since the sensitivity is not pressure dependent.

CONCLUSIONS

It must be pointed out that while the pressure dependence of the R_1 line has been accurately characterized with respect to frequency and wavelength shift, it can only be applied in the strictest sense to a measurement made in a hydrostatic environment. In principle, the pressure can be specified accurately to 200 kbar. In practice, however, one has to consider that nonhydrostatic effects arise above 104 kbar. The magnitude of these nonhydrostatic effects and how they influence accuracy in the pressure measurement depend upon the particular pressure transmitting medium and pressure generating system under consideration. If fluids are used, then, of course, these effects arise only after the fluid has become a glass and the magnitude of the effect naturally increases the further one goes into the glassy state with increasing pressure. When solid pressure transmitting media are used, allowance must be made for nonhydrostaticity which should be reflected in the uncertainty assigned to the pressure value. Our data presented here above 104 kbar indicates that the shift of the center of the R_1 line is a measure of the average pressure, as measured by x-ray diffraction, using the same calibration as if the medium were hydrostatic.

The linear relationship obtained in this work relative to pressures determined using Decker's equation of state for NaCl (and thus suggested for true pressures) suggests the use of the ruby R_1 line shift as a secondary standard pressure scale. This would require a calibration using a primary pressure standard measurement at lower pressures. Such an approach is much more appealing than the NaCl compression because the measurement sensitivity is higher, the procedure is much more rapid, and high-pressure equipment with optical access is more prevalent than equipment with x-ray access. Furthermore, if the current experiment is taken as evidence of linearity, only one measurement is required to determine the slope of the calibration curve. Following the example of the Practical Temperature Scale, it appears meaningful to define a pressure scale (until a primary standard, force/area, measurement can be made) as those pressures obtained from a linear relationship between wavelength shift of the R_1 line and pressure. If such an approach were to be taken, the accuracy with which the slope $dp/d\lambda$ can be determined would be limited by the inability to measure $\Delta\lambda$ at the lower pressures with precision consistent with the pressure measurements. For example, if the calibration were made against a Free Piston Gauge at 25 kbar (maximum pressure to which this gauge has been operated), the uncertainty of 0.2 Å quoted here would give an uncertainty greater than 2.2% in $dp/d\lambda$. It, of course, is possible to increase the accuracy of the line-shift measurement to some extent. If measurements using a piston-cylinder apparatus to 50 kbar were used as a standard (for example, the work of Haygarth *et al.*[8,9]) where pressure measurements accurate to 0.5 kbar are claimed at 50 kbar, $dp/d\lambda$ could be determined to an accuracy approaching 1%. In either of these two feasible examples, it appears with present state-of-the-art techniques it would be difficult to determine the absolute pressure vs $\Delta\lambda$ shift with an accuracy better than approximately 1%. This is, however, a significant improvement over the accuracy on an absolute basis provided by the equation of state of NaCl at the higher pressures.

In summary the following conclusions can be made:

(i) The pressure dependence of the R_1 ruby fluorescence line is linear with respect to wavelength and energy (wave number) to 195 kbar when calibrated against the compression of NaCl using the Decker equation of state.

(ii) The values of the slopes at 25 °C are (a) $dp/d\lambda = 2.740$ kbar/Å and (b) $dp/d\bar{\nu} = -1.328$ kbar/cm^{-1}, in agreement with previously reported values.

(iii) In principle, the pressure can be accurately specified to 195 kbar. In practice, however, nonhydrostatic effects come into play above 104 kbar and the magnitude of these effects and their influence on accuracy depend on the pressure transmitting medium and pressure generating system under consideration.

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