The ruby pressure standard to 150 GPa

Akobuije D. Chijioke, W. J. Nellis, A. Soldatov,^{a)} and Isaac F. Silvera^{b)}
 Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138

(Received 14 February 2005; accepted 13 October 2005; published online 8 December 2005)

A determination of the ruby high-pressure scale is presented using all available appropriate measurements including our own. Calibration data extend to 150 GPa. A careful consideration of shock-wave-reduced isotherms is given, including corrections for material strength. The data are fitted to the calibration equation $P=(A/B)[(\lambda/\lambda_0)^B-1]$ (GPa), with $A=1876\pm6.7$, $B=10.71\pm0.14$, and λ is the peak wavelength of the ruby R1 line. © 2005 American Institute of Physics.
 [DOI: 10.1063/1.2135877]

I. INTRODUCTION

In this paper we examine the ruby pressure standard at very high pressures generated in diamond anvil cells (DACs) and present a calibration taking into consideration two data sets in the literature and our own data. For the calibration we utilize experimental data that we have collected to ~ 100 GPa, data from Dewaele *et al.*¹ to 150 GPa, and data from Zha *et al.*² to 50 GPa. All of these data sets were collected in quasihydrostatic media. As discussed below, most of the data for pressure determination are based on the equations of state of metals from shock waves (shock-wave-reduced isotherms or SWRIs reduced to 300 K). In our calibration we use SWRIs described in another article.³ These SWRIs have been derived from the best available Hugoniot data with state-of-the-art thermal corrections and are corrected for material strength, where such data are available.

There are two main ways that pressure has been measured in DACs: the calibrated ruby fluorescence line shift with pressure and x-ray diffraction of a pressure marker, i.e., a metal with a well-known relationship between pressure and volume, with the molar volume being determined from x-ray-diffraction measurements. The advantage of the ruby method is that it is quick, easy, and can be done on a bench top in any laboratory with a laser and a spectrometer; micron-sized ruby grains can also be distributed throughout the pressure medium to give an indication of the uniformity of the pressure. The current limitation is that it has only been calibrated in a useful way to 80 GPa, the so-called quasihydrostatic ruby scale, by Mao *et al.*⁴ and researchers have been using uncontrolled extrapolations up to the 300+ GPa (3 Mbars) range. The method of using markers to calibrate ruby was introduced by Piermarini *et al.*⁵ using the Decker⁶ equation of state (EOS) of NaCl as the pressure standard up to 19.5 GPa at 300 K. Later Mao *et al.*⁷ extended the marker method to the megabars range at 300 K using SWRIs. Most of the data in our analysis continue with the use of this marker method as the most reliable method of producing a calibration based on the experimental determination of pressure.

There are experimental issues associated with both techniques, i.e., ruby and x-ray markers. Pressure can be measured very accurately at low pressures to ~ 100 bars (10 MPa) precision with good temperature regulation.⁸ Ruby becomes difficult to measure in the megabar-plus pressure range as the signal weakens and is masked by fluorescence from the diamond anvils, but important techniques have been developed to alleviate this problem.^{9,10} The x-ray marker technique has the advantage that it directly measures a calibrated material with no practical limitation to the pressure range. However, the x-ray-scattering signal is quite weak and to efficiently measure pressure, the photon flux of a synchrotron is required. If this were the only technique for pressure determination, high-pressure research that now flourishes in tabletop environments would be limited to those with access to synchrotrons and progress would be severely limited. A second disadvantage exists for multimegabar pressures: the size of the diamond culets are reduced and thus the diameter of the hole in the gasket containing the sample. It then becomes difficult to separate the marker x-ray signal from the large background due to the x-ray-diffraction signal from the gasket. This problem is greatly alleviated in third-generation synchrotrons where x-ray beam diameters can be reduced to several microns. A variation of this method is to x-ray the edge of the metallic gasket as the marker and assume that this is representative of the sample pressure, after corrections. By contrast, ruby grains of the order of 1 μm in dimension do not suffer this problem.

Thus, it is currently vital to accurately extend the range of the calibrated ruby scale. A striking example of the need comes from studies of hydrogen at high pressures. Narayana *et al.*¹¹ studied hydrogen in a DAC to 342 GPa and observed that the sample remained transparent to this pressure (the only measurement made on the sample was this visual one). Later, Loubeyre *et al.*¹² studied hydrogen and observed it to become black at a lower pressure, 320 GPa. Two possible solutions to these contradictory results are that Narayana *et al.* did not have a sample in their DAC gasket, but they are confident that they did,¹³ and that the pressure scales were incorrect so that the sample of Loubeyre *et al.* was really at a higher pressure than that of Narayana *et al.* Narayana *et al.* used the x-ray-marker method and determined the pressure from that of the gasket adjacent to the sample, making a

^{a)}Present address: Department of Applied Physics and Mechanical Engineering, Lulea University of Technology, SE 971 87 Lulea, Sweden.

^{b)}Electronic mail: silvera@physics.harvard.edu

correction to the pressure in the gasket because it was not embedded in the hydrogen sample. Loubeyre *et al.* used the ruby scale to around 200 GPa, but were unable to measure the signal at higher pressures as it weakened. They then measured the shift of the first-order Raman-active phonon of the diamond in the culet region and estimated the pressure from a Gruneisen expansion for the EOS of diamond. Neither of these techniques is conventional nor calibrated and the uncertainty might be lifted if both groups had used the same method to measure the pressure. Indeed, extrapolation of the ruby calibration to 350 GPa could be in error by more than 15%, as we shall see, and could explain this conflict. There has been subsequent work to calibrate the diamond phonon up to 300 GPa.¹⁴

Following this Introduction we review the existing calibrations of ruby. We then discuss the use of SWRIs, the pressure scale, and the ruby spectra.

II. PREVIOUS RUBY PRESSURE SCALES

Ruby (Cr³⁺-doped Al₂O₃) has played a central role in high-pressure physics. The proposal by Forman *et al.*¹⁵ that the pressure shift of the ruby *R* lines (*R*₁ and *R*₂) could be used to measure pressure in DACs led to the widespread use of the DAC as a quantitative scientific tool. The simple excitation of ruby with a laser, typically in the green or blue, and the optical observation of the fluorescence spectrum have been adopted by the high-pressure community as one of the standard methods of measuring pressure. Calibrations of ruby are carried out by placing ruby in a pressure cell along with a sample of another material with a known pressure scale, the marker, and transferring the scale to the shift of the ruby *R* line. It is vital that the ruby and the calibrant should be in a hydrostatic pressure medium to obtain a reliable calibration. At high pressures all materials solidify and thus can develop shear strength, leading to nonhydrostatic conditions.

The best quasihydrostatic high-pressure media are helium and hydrogen, remaining so to megabar pressures. Neon is probably a reasonably quasihydrostatic medium, but has not been studied for this property to high enough pressures. Surprisingly, xenon has been found to be quasihydrostatic¹⁶ to about 1 Mbar; this is probably because of a sluggish fcc-hcp phase transition that takes place over a large pressure range.¹⁷ In our measurements, to be described, we have used helium, hydrogen, and xenon as quasihydrostatic pressure media.

Piermarini *et al.*⁵ calibrated the shift of the ruby fluorescence spectrum against pressure to 19.4 GPa, transferring the Decker⁶ sodium chloride pressure scale at 300 K to ruby. Decker's EOS was normalized to agree with the measured thermal-expansion coefficient and adiabatic bulk modulus at zero pressure and his calculated Hugoniot agrees with the measured one up to 25 GPa. Piermarini *et al.* found a linear relationship between the wavelength shift of the ruby *R*₁ line and pressure. Both ruby and NaCl were embedded in a 4:1 methanol-ethanol mixture used as a quasihydrostatic pressure medium. Subsequently, Ruoff and Chhabildas¹⁸ and Brown¹⁹ presented improvements in the Decker scale that would affect this calibration, increasing the slope of the pres-

sure versus wavelength-shift curve. Although 4:1 methanol-ethanol has been used as a quasihydrostatic pressure medium at low pressures, it undoubtedly becomes nonhydrostatic at higher pressures.

As the pressure range accessible to DACs rapidly increased, Mao *et al.*⁷ extended the ruby scale to 100 GPa. In this method the markers are metals (Cu, Mo, Pd, and Ag) for which the equation of state (pressure/volume EOS) at 300 K has been derived from shock-wave measurements. One or more markers are placed in a DAC along with grains of ruby and the ruby spectrum is measured along with an x-ray-diffraction spectrum of the markers from which the volume, and thus the pressure, is determined. In this work 4:1 methanol-ethanol was used as the pressure medium. A small deviation from the linear behavior found by Piermarini *et al.* was observed and pressure was fitted to the equation

$$P = \frac{A}{B}[(\lambda/\lambda_0)^B - 1](\text{GPa}), \quad (1)$$

where λ is the measured wavelength of the ruby *R*₁ line, $\lambda_0=694.24$ nm is the zero-pressure value at 298 K (*R*₂ is at 692.81 nm), and $A=1904$ and $B=5$ are the least-squares-fit parameters. We shall call this calibration MBSS78. This was extended to 1.8 Mbars, the highest pressure calibration to date, by Bell *et al.*²⁰ using gold and copper markers. Powdered gold and copper were covered with crushed ruby in the DAC and pressurized. This calibration (BXM86) is also known as the nonhydrostatic ruby scale, as there was no other pressurization media in the cell; the fit parameters to Eq. (1) were $A=1904$ and $B=5$, the same as with MBSS78. We note that for the pressure determination from gold they used the EOS of Heinz and Jeanloz.²¹ Heinz and Jeanloz determined the room-temperature EOS of gold using x-ray diffraction for the volume and the MBSS78 ruby calibration was part of their input for the pressure. Thus, this calibration is based on a "circular" use of data and does not meet the requirements for a standard. The Heinz-Jeanloz room-temperature EOS of gold to 200 GPa is partially based on a pressure calibration that is no longer used and should be considered with caution.

Mao *et al.*⁴ also calibrated ruby in argon (MXB86) (considered to be a quasihydrostatic pressure medium) to 80 GPa using copper and silver markers and found fit parameters to Eq. (1) of $A=1904$ GPa and $B=7.665$. For a given wavelength shift this gives a higher pressure than for the nonhydrostatic scale, suggesting that nonhydrostatic pressure media can profoundly affect the calibration. We note that Boppart *et al.*²² had already pointed out that argon becomes nonhydrostatic above 12 GPa; this suggests that further adjustments to the ruby scale carried out in a quasihydrostatic medium might be required. In a study of neon to 110 GPa, using a tungsten marker, slight deviations from the quasihydrostatic scale were found by Hemley *et al.*²³ These yielded higher pressures for a given wavelength shift, but the authors did not give fit parameters to Eq. (1). One might expect neon to be weaker than argon and thus more quasihydrostatic; the authors of this work found such indications, but the quasihydrostaticity of neon has not been studied well.

In x-ray-diffraction and Raman-scattering studies of diamond compressed with a helium pressure medium, Aleksandrov *et al.*²⁴ found discrepancies when they used the ruby pressure scale MBSS78. They presented a ruby calibration based on the extrapolation of the diamond EOS from low-pressure ultrasonic data. Fitting to Eq. (1) they found $A=1918$ and $B=11.7$; we call this AGZS 87. The earlier calibration (MBSS78) was based on experimental equations of state from shock-wave compression of metals. This is a fundamental method for determining pressure on a Hugoniot; however, it has to be reduced to ambient temperatures for calibration purposes. On the other hand, the diamond calibration, while interesting and indicating a possible problem with the ruby scale, is not based on any primary standard or experimental data relating pressure to volume at high compression. Due to the small compressibility of diamond, the P - V isotherm extrapolated from accurate ultrasonic measurements of K_0 and K'_0 may give a fairly accurate reference curve up to ~ 100 GPa. However, the present uncertainty in the ultrasonic value limits accuracy at higher pressures.²⁵

Zha *et al.*² combined the results of Brillouin scattering and x-ray diffraction to make absolute measurements of the EOS of MgO and to calibrate ruby to 55 GPa on this primary scale (ZMH00) to 1% accuracy. They fitted their data to Eq. (1) with the initial slope fixed, i.e., $A=1904$ GPa, and found a value of $B=7.715$. This scale shows good agreement with the earlier low-pressure data, but indicates that at the high-pressure end of the calibration the pressure is higher than in MXB86.

Holzappel²⁶ has considered x-ray data on diamond²⁷ in a He pressure medium with ruby to pressures up to 140 GPa. He proposed to use the ultrasonic values for the zero-pressure bulk modulus K_0 and its isothermal pressure derivative K'_0 to obtain an EOS for diamond by extrapolating these zero-pressure values up to ~ 100 GPa with a theoretical phenomenological EOS and then adjusted the ruby pressure shifts to match this extrapolation. He finds, using Eq. (1), $B=10.8$ with $A=1904$; we call this H03. Holzappel also concluded that B might be as large as 15 if A is reduced significantly. He also proposed a three-parameter functional form for fitting of the ruby scale that gives more flexibility for high pressures, but lacking very-high-pressure data at this time, we find that the form of Eq. (1) is adequate.

Kunc *et al.*²⁸ calculated the pressure-volume relationship of diamond up to 600 GPa. They used their calculated zero-pressure bulk modulus and its pressure derivative to fit their P - V data with a phenomenological EOS and also presented comparisons to the HO3 ruby scale. They suggest fit parameters $a=1820$, $b=7.9$, using the quadratic form of Eq. (2). We call this KLS03. These papers using diamond as a reference material pointed out possible serious discrepancies arising from the MXB86, but we do not use data from HO3 or KLS03 since diamond has not been established as a standard.

Dorogokupets and Oganov²⁹ analyzed the isotherms of Cu and Ag used in MXB86. They then reanalyzed the data from that calibration in argon to find $A=1871$ and $B=10.06$. We call this DO03.

The most recent and complete set of data is from Dewaele *et al.*¹ They calibrated Cu, Al, and W against ruby

FIG. 1. Comparison of various earlier ruby scale calibrations and their extrapolations to higher pressures. The sources of the curves are identified.

to 150 GPa and Au, Pt, and Ta to just under 100 GPa. Samples were in a helium pressure medium at room temperature along with one chip of ruby. This data set contains the highest pressures yet for a calibration of ruby in the best-known quasihydrostatic pressure medium and appears to be of very high quality. In comparing with the shock-wave-reduced pressures (see ahead) they found a systematic deviation of the pressures based on MXB86 of Mao *et al.* To correct this they used Eq. (1), fixed the A parameter at 1904 GPa, and adjusted B to 9.5. Using this calibration scale, a deviation plot with respect to the SWRI pressures, the results obtained for several markers do not show a global systematic deviation as was the case with MXB86; we call this DLM04.

Several of the calibrations discussed are compared in Fig. 1. As a point of interest we display these to very high pressures to demonstrate how large the error might be with an extrapolation, all in the form of Eq. (1). In the remainder of this article we focus on a calibration of ruby using what we consider to be the most reliable, fundamental sets of experimental data in quasihydrostatic media: the data of Zha *et al.*,² where pressures are derived from thermodynamic relations between measured properties of MgO in helium; the extensive data of Dewaele *et al.*,¹ who used the room-temperature isotherms of six metals in helium reduced from shock-compression data; and our own data in quasihydrostatic media, also using shock-wave-reduced pressures. We collect all of this data for ruby shifts and calibrate with recently developed isotherms presented in another article.³

III. OUR RUBY CALIBRATION DATA

Our initial objective was to extend the ruby calibration into the 200+ GPa pressure range in a quasihydrostatic medium. We loaded markers of gold and platinum in helium, hydrogen, and xenon, along with grains of ruby, at Harvard

FIG. 2. An example of ruby spectra from micron-sized grains in solid helium and xenon at room temperature at indicated pressures. A strongly broadened spectrum of xenon due to a nonhydrostatic pressure distribution at a pressure of 107 GPa is shown.

University and transported them to the synchrotrons at CHESS in Ithaca, NY and NSLS in Brookhaven, NY. The ruby spectra were measured before and after the x-ray-diffraction spectra to ensure that the pressure was stable (loss of pressure medium and thus pressure can occur via diffusion of light atoms and molecules into the gasket and diamond). An example of a ruby spectrum in solid helium is shown in Fig. 2. Peak wavelengths or frequencies of the ruby *R* lines were determined by fitting to Lorentzian functions. Due to the relatively narrow spectra the same result was found for fitting in wavelength or frequency. In general an optical spectrometer does not have a flat transfer function and the broad spectra can be distorted. The ruby lines are narrow enough that there is not a significant pulling or shifting of the line peak that requires procedures to correct the spectrum.

There are two methods that we used to check the quality of the pressure: (1) measure the pressure in a distribution of ruby grains in the gasket hole and (2) measure the spacing between the *R*1 and *R*2 ruby peaks, which is expected to remain constant for hydrostatic pressures and to shift in the presence of deviatoric stresses. The spectra from ruby grains at two different locations in the xenon sample at 57 GPa indicated a pressure difference of 1.5 GPa. In Fig. 3 we show the peak spacing for some of our samples. Clearly this spacing is well preserved with increasing pressure for helium and hydrogen, whereas deviations occur for xenon. The splitting in xenon increases above 100 GPa indicating nonhydrostaticity in xenon above 100 GPa. An additional indication of nonhydrostatic pressure is the broadening of the ruby lines. We show an example of broadened lines in xenon in the nonhydrostatic region, also in Fig. 2.

Normally we cryogenically load DACs with helium and hydrogen and have had pressures reaching between 200 and 300 GPa before failure. Due to experiencing failure of diamonds at high pressures and room temperature, we always try to maintain our DACs around liquid nitrogen tempera-

FIG. 3. The splitting of the ruby *R* lines as a function of pressure for helium, hydrogen, and xenon pressure media.

tures (~ 77 K) or lower when loaded with quantum solids such as hydrogen or helium. Our procedure for the ruby calibration runs was to load the DACs, warm them to room temperature, carefully pack the DACs in shock-absorbing containers, and transport them to a synchrotron. None of our loaded DACs achieved pressures above 120 GPa. We suspect that these problems arose from diffusion of helium or hydrogen into the diamonds, which were embrittled and failed at lower-than-design pressures. Dewaele³⁰ also suffered from helium embrittlement, but succeeded in studying three metals that achieved higher pressures. We considered our hydrogen calibration points to be of high quality. Xenon gave reasonable quasihydrostatic results up to 90 GPa, but higher-pressure points were initially omitted due to development of nonhydrostaticity. Finally, we decided to omit all of our data points using xenon as a quasihydrostatic pressure medium from the ruby calibration due to evidence of a small nonhydrostatic component of the pressure below 100 GPa. We show all of the xenon data in later figures but omit these points from the calibration.

Our helium data were of high quality in terms of the ruby and x-ray spectra and utilized both platinum and gold markers, but the data were shifted substantially from other data sets. A close review of the data showed that we did not measure the zero-pressure spectrum of ruby for that run and suspect that there may have been a calibration problem in the optical spectrometer; this data has been omitted from the fit. As a consequence we have a paucity of usable data points, given in Table I. The largest number of high-pressure data points that will be used for the calibration are from Dewaele *et al.* In Fig. 4 we plot all of our data and compare them with the data of Dewaele *et al.* When our calibration studies began, gold seemed to be a popular and attractive x-ray marker. After finishing our measurements and an extensive analysis (see later) we conclude that Au was not the best choice for a marker and Cu, W, or Ta are better markers.

TABLE I. Data from our calibration runs using hydrogen and xenon pressure media on gold markers.

Medium	$\Delta\lambda$ (nm)	$\sigma(\Delta\lambda)$ (nm) ^a	Au (V/V_0) ^b	Au $\delta(V/V_0)$ ^c
Xe ^d	7.91	± 0.03	0.9073	0.0011
	16.51	± 0.09	0.8432	0.0065
	19.51	± 0.04	0.8301	0.0056
	21.49	$\pm 0.40^e$	0.8127	0.0044
	24.67	± 0.05	0.8017	0.0034
	24.89	± 0.04	0.7968	0.0045
	27.61	± 0.11	0.7754	0.0024
	33.79	± 0.10	0.7569	0.0022
	35.02	$\pm 0.30^e$	0.7512	0.0015
H ₂	23.61	± 0.002	0.7891	0.0018
	24.56	± 0.007	0.7886	0.0044
	26.30	± 0.02	0.7749	0.0033

^aStandard deviation of fitted peak center.^bAverage value from four x-ray peaks.^cMaximum difference between averaged volume from four x-ray peaks and volume from individual x-ray peaks.^dThese points are not included in the fit.^eWeak ruby spectra obtained.

IV. PRESSURE STANDARDS

We shall present a ruby-standard pressure scale. Ideally, pressure calibration would be determined in a measurement that directly gives pressure, along with the ruby spectrum. This is the case for MgO; however, that work yielded an absolute pressure scale only up to 50 GPa. X-ray markers use SWRIs as the reference pressure for several metals that are used in the calibration (Cu, W, Al, Au, Pt, and Ta). These SWRIs are derived from measured P_H - V curves achieved by shock compression, called Hugoniot, where P_H is the shock pressure and V is the molar volume. Temperature can increase substantially under adiabatic shock compression. In

TABLE II. Parameters for the SWRIs for metals used in this ruby pressure calibration. The Vinet form, with $X=V/V_0$, is $P_{300}(X)=3K_0[(1-X^{1/3})/X^{2/3}]\exp[\eta(1-X^{1/3})+\beta(1-X^{1/3})^2+\xi(1-X^{1/3})^3+\delta(1-X^{1/3})^4]$.

Element	K_0	η	β	ξ	δ
Al	72.6	4.1267	26.1269	-154.33	326.69
Cu	133.3	5.4167	15.921	-90.223	235.81
Ta	194.1	1.9265	52.348	-402.72	1031.5
W	308.6	2.7914	45.694	-409.97	1290.2
Au	177.26	6.3800	1.9334	-1.0292	33.941
Pt	280.03	6.3289	-1.3811	61.492	-156.48

principle the pressure and volume in a shock-compressed material can be determined absolutely and very accurately. Thus, a SWRI is a pressure-volume (or density) EOS curve at a fixed temperature derived from a shock-compression curve at high pressures and temperatures. We consider SWRIs for markers at $T=300$ K. These markers can be x-rayed at room temperature to determine the density and thus the pressure. In Ref. 3, Chijioke *et al.* have carefully considered the Hugoniot for Cu, W, Al, Au, Pt, and Ta. Shock compression is extremely rapid. For solid metals at 100 GPa, shock pressure, which has a rise time of the order of picoseconds, induces a high density of lattice defects, which in turn increases shear strength. A shocked solid has three principal directions. The longitudinal direction is parallel to the direction of shock propagation and the transverse directions are mutually orthogonal to each other and to the direction of shock propagation. Measured Hugoniot pressures of solids are actually normal stresses in the direction of shock propagation. Stress is dominated by pressure, the average of the three principal stresses, plus a small component caused by strength. X-ray markers in a DAC are compressed slowly and quasi-hydrostatically, which is expected to cause less defect formation and a lower material strength increase.

For compression in a hydrostatic medium, the state achieved in the marker is hydrostatic, even if the solid embedded in the pressure medium itself has strength. Thus, the strength of metal x-ray markers in a pressure medium can be neglected in a DAC. Shock-induced shear strength must be subtracted from measured Hugoniot stresses of a solid to obtain the Hugoniot corresponding to a hydrostatic or "fluid" metal marker, as appropriate for a DAC. For this reason, available literature values of shock-induced strength as functions of shock pressure were subtracted from measured Hugoniot stresses of solid metals to obtain the Hugoniot corresponding to a fluid. These fluid Hugoniot were then reduced to the 300 K isotherms using state-of-the-art corrections for the thermal pressure³¹ and fitted to a Vinet curve³² for convenience of interpolation. The Vinet parameters are presented in Table II. We stress that this parametrization of the SWRIs is for use in interpolation of P , V points up to the indicated pressure limits and the parameters are given to five decimal places for numerical accuracy. A deviation plot of the Vinet fit and the data in Ref. 3 show that the values represent the input data to high accuracy.

V. THE CALIBRATION

We have fitted all of the data to Eq. (1). These include our own data set, that of Dewaele *et al.*, and that of Zha *et al.*

FIG. 4. Ruby calibration data using a gold marker and hydrogen and xenon pressure media, compared with data from Dewaele *et al.* in a helium medium. The fit is used as a guide to the eye.

FIG. 5. Deviations of the MXB86 and DLM04 scales using Form I [Eq. (1)] showing that the new fit, CNSS05, predicts higher extrapolated pressures. We also show the approximate error band for the new fit on the horizontal axis at the one-sigma level for the A and B constants. The error band shown is conservative such that correlations between the fitted A and B values are not taken into account. The dotted curve is a deviation plot using the quadratic fit, Form II.

For the data of Dewaele *et al.*, using their reported results, we extracted the ruby $R1$ wavelength shift as a function of the compression, $X = V/V_0$, where V_0 is the ambient pressure molar volume, and obtained the pressure from the SWRI of the particular metal marker at X . We have performed a non-linear least-squares fit to these data and find the coefficients $A = 1876 \pm 6.7$ and $B = 10.71 \pm 0.14$, where errors are the standard deviations from the fit. We call this scale CNSS05. We have given the gold and platinum markers a weighting factor of 0.5 in the fit because there are no data available in the literature for the shock-induced strength of gold and platinum and because of the paucity of Hugoniot data points for gold. Note that the data for both of these markers only extend to ~ 100 GPa. We show a plot of the deviation of the so-called quasihydrostatic scale MXB86 from our pressure scale, CNSS05, in Fig. 5. MXB86 has been the standard used for almost all megabar-pressure experiments by extrapolation. We also compare our scale to the recent proposal of Dewaele *et al.*, DLM04, extrapolating to 400 GPa to show the differences between these scales.

As pointed out by Holzapfel²⁶ and indicated by the measurements of Grasset,⁸ the linear calibration to 20 GPa of 2.74 GPa/nm⁵ [corresponding to an A value of 1904 GPa in Eq. (1)], which has been kept as the initial slope in most subsequent calibrations, is probably higher than the initial slope. In fitting we have allowed both A and B to vary, obtaining an A value of 1876 GPa.

A deviation plot of the pressure difference between the pressure for each marker and our scale versus our scale pressure, shown in Fig. 6, best displays the quality of the fit. Although there are small systematic deviations for various markers, in general the deviations are quite reasonable, considering the uncertainties in the SWRIs. Slight exceptions are Al and Au. There are a large number of measured points in

FIG. 6. Pressure deviations of the marker standards from the new fit to the $R1$ line shift. Au_1 is from Dewaele *et al.*; Au_2 is our data in H_2 . Au_3 is our data in Xe. Au_3 was not used in doing the ruby fit. The dashed line shows a deviation plot of a fit to the Al data alone, indicating that the two-parameter-fitting formula used is adequate for any of the metals used in the overall fit. One sigma error bars are shown for selected Al and Cu data points.

the literature for the Hugoniot of Al with good overlap, so these data must be highly regarded. Al has a 5% deviation from the pressure scale at 150 GPa and the uncertainty for pressure in the Al Hugoniot at a compression corresponding to this pressure on the isotherm is $\sim 1.2\%$ at the one-standard-deviation level.³³ At a shock pressure of 140 GPa, Al is melted³⁴ so that there is no strength correction here. Thus, experimental errors in the Al Hugoniot and shock-strength data are small compared to the total deviation at 150 GPa. A more flexible form of the fitting formula cannot correct the deviations. As an example we show the fit to the Al SWRI data alone (dashed line) in Fig. 6, and the deviations of the Al data about this line are quite random.

Dewaele *et al.* report fractional uncertainties on their pressures ranging from 5% at low pressures to 1.3% at 150 GPa. Systematic errors probably account for the remainder of the deviations. Because the He pressure medium is solid with some shear strength, He could support a small pressure gradient, perhaps a few gigapascals at the highest pressures. Although Dewaele *et al.* report no evidence of nonhydrostatic stresses in He up to 150 GPa, this was a non-quantitative determination. Lorenzana *et al.*³⁵ studied the pressure distribution in (quasihydrostatic) hydrogen at ~ 150 GPa and ~ 77 K and measured a variation of 8 GPa using a distribution of ruby grains. Thus, it is possible that the pressure markers in helium were not all at the same pressure. Since there was only one ruby chip in each DAC, reported in Ref. 1, the pressure distributions in the helium were not measured. A possible 1%–2% variation in pressure caused by shear strength in He at 150 GPa and room temperature might be reasonable. Another source of error might be the thermal pressure. The correction in Al is relatively large (50 GPa at 150 GPa³ on the isotherm) so that uncertainties in calculated thermal pressures of $\sim 6\%$ might account for the Al deviation from the fit to all the data. [Note:

To get a $\sim 2\%$ variation in 150 GPa (3 GPa), the uncertainty in calculated thermal pressure (~ 50 GPa) is $\sim 6\%$. Finally, Al is melted and thus has no strength correction at the higher pressures, while copper and tungsten do; the strength data in the literature did not provide uncertainties. Thus, a deviation in pressure of $\sim 5\%$ for Al at 150 GPa is not unreasonable. In Fig. 6 we show $\pm$ one-sigma deviations for two of the metals, aluminum and copper, at a few pressure points. The errors included x-ray volume, Hugoniot stress, an estimate of the strength correction, an estimate of the thermal pressure error, and ruby line shift; uncertainties were treated as uncorrelated.

We note that Dewaele *et al.* used calculated data from an underground experiment on Al for their ruby calibration.³⁶ The Al isotherm was extracted from an EOS of Al calculated by Moriarity; this was used as a reference material to interpret shock-impedance match experiments in close proximity to underground nuclear explosions. The uncertainty in Al pressure at a given volume on that isotherm was estimated to be $\pm 10\%$.³⁶ These are not absolute Hugoniot measurements, such as those in Mitchell and Nellis,³³ used here, in which no theoretical model is used, and therefore the same accuracy is not expected. These two isotherms differ by 15.5 GPa at 150 GPa; using the underground isotherm as was done in Ref. 1 would give a negative deviation for Al in Fig. 6, rather than positive. Gold shows some deviation on the low side, but the Hugoniot of Au has more uncertainty and it has not been strength corrected. However, the strength correction would increase the deviation. The ruby data from xenon seem to have a larger deviation that we suspect is a problem with the hydrostaticity for these points. The most important points for the calibration are the high pressure points of Al, Cu, and W. Considering the uncertainties in pressure indicated by using several metal markers, the use of several markers is the best way to calibrate the pressure scale at the present time.

High-pressure measurements beyond the region of calibration traditionally extrapolate and quote the scale so that when an improved scale is available a correction can be made. To the extent that the scale presented here can be extrapolated, we see from Fig. 5 that at 400 GPa on our scale, the old MXB86 scale would give a pressure 67 GPa lower, or 333 GPa. Perhaps this explains the conflict between Narayana *et al.*¹¹ and Loubeyre *et al.*¹² on hydrogen at high pressures.

VI. DISCUSSION

A. Ruby

In our calibration the chromium atomic percent in ruby was specified as 0.5. At this concentration there can be a weak N_2 line (pair spectrum from fourth neighbor Cr^{+3} ions).³⁷ At lower concentrations these spectra disappear, but the R -line signal reduces proportionally; at higher concentrations pair spectra become too strong and the R lines broaden. Ruby pressure determination becomes more difficult to use in the multimegabar pressure region, but still enables tabletop experiments to reach extremely high pressures without the need of a synchrotron. In the megabar pressure range the

signal becomes weak and obscured by background fluorescence. Eggert *et al.*³⁸ have presented a scheme for the most efficient way of pumping ruby at high pressures and a method to reduce the diamond fluorescence background using time-resolved spectroscopy.⁹ Chen and Silvera¹⁰ have shown how to pump and observe the ruby line with a technique that should be useful to ~ 500 GPa. Thus, as pressures go higher we expect that ruby will continue to play an important role.

As temperatures are lowered below room temperature there is a shift in the line frequency which levels off at about 100 K, but this is easily taken into account.^{39–41} Chai and Brown⁴² point out that the $R2$ line is insensitive to nonhydrostatic pressures, while the $R1$ is. One might consider using the $R2$ line; however, $R1$ and $R2$ lines are thermalized and at liquid helium temperatures only the $R1$ fluoresces. We considered the use of the $R2$ line for xenon, or $R2$ plus the zero-pressure splitting of the $R1$ and $R2$, but this did not significantly improve the deviation of the xenon data.

It remains important to extend the ruby calibration to still higher pressures. We believe that this can be implemented with a DAC using a helium pressure medium, but maintained at low temperatures at all times to suppress diffusion. In the meantime the procedure of extrapolating the scale and noting the scale used will remain a useful practice.

B. Extrapolations

The present form of the ruby calibration fitting formula given by Eq. (1) is *ad hoc*, as it is not based on an expected variation of the energy levels of ruby with pressure. It works well in fitting the data because the shift of the ruby $R1$ line is almost linear with pressure, with a small nonlinear correction. One might also choose to fit to a quadratic equation of the form, which we call form II,

$$P = a \left[\left(\frac{\lambda - \lambda_0}{\lambda} \right) + b \left(\frac{\lambda - \lambda_0}{\lambda} \right)^2 \right]. \quad (2)$$

Doing so fits the data up to 150 GPa equally well as Eq. (1) does, with $a = 1798 \pm 8.4$ and $b = 8.57 \pm 0.15$. This extrapolates to a lower pressure at 300 GPa than does Eq. (1). For example, at 333 GPa on the MXB86 scale, the pressure using Eq. (2) would be 359 GPa.

C. Shock and isentropic compression

Dynamic compression measurements will continue to provide experimentally based P - V paths on which to base pressure scales for static compression to pressures substantially higher than the 150 GPa limit considered here. However, errors involved in the reduction process need to be better understood and treated with greater care above 150 GPa. Causes of the deviations in pressure given by various metal markers, illustrated in Fig. 6, need to be determined. Hugoniot data measured to date for Al, Cu, Ta, and W are of sufficient accuracy for pressures up to 400 GPa. High-quality Hugoniot data for additional metals, such as Mo, Pt, and Au, are also needed for systematic comparisons and

much of these data are already available. However, strength measurements along the Hugoniot to above 200 GPa are needed for Ta, W, Mo, Pt, and Au.

Error bars in future shock-wave experiments are particularly important for calibration purposes. Shock temperatures are getting larger above 150 GPa, which means that calculated thermal pressures are becoming a larger component of shock pressure, as well as thermally softening these strong metals. So the accuracy of thermal-pressure calculations and understanding the interplay between strength and temperature need to be improved. The fundamental limit for use of Hugoniots as reference curves is that at some high pressures, compressibilities are reduced substantially because of ever increasing shock temperatures.

In recent years, dynamic isentropic compression curves have been measured for metals that are used as pressure markers,⁴³ which offer reference curves to derive 300 K isotherms at ~ 150 GPa pressures and higher. Thermal pressures separating isentropes from 300 K isotherms are generally significantly smaller than those between Hugoniots and 300 K isotherms. However, strength induced by isentropic dynamic compression is substantially greater than along the Hugoniot. In the case of W, for example, yield strengths on the isentrope and Hugoniot at 150 GPa are ~ 8 and 1.5 GPa, respectively.⁴³ Presumably, a major cause of the difference is that temperatures and thermal softening of strength differ greatly in the two cases. In actuality, P - V curves of solids measured under dynamic isentropic compression are not quite reversible, and thus not quite isentropic, because of material strength. They are called isentropic because the rise time of pressure is sufficiently slow that the process would be isentropic for a fluid sample. The differences between pressure-density curves on application of dynamic pressure and pressure-release curves are a way to determine material strength under isentropic loading.

In the future, when more isentropic compression curves and strengths along these curves are measured and when the interplay between dynamic strength and temperature are better understood, then isentropes can serve as reference curves for pressure calibrations, analogous to the way Hugoniots have been used. In fact, at shock pressures above ~ 300 – 400 GPa, shock temperatures become so large that thermal pressures become much larger than on the 300 K isotherm and limit shock compression to approximately four fold of the initial density.⁴⁴ In contrast, temperatures and thermal pressures achieved by dynamic quasi-isentropic compression are substantially lower than on the Hugoniot and isentropic compression does not have such a fundamental limit. Thus, reductions of experimentally determined isentropes to isotherms might well be the most accurate way to develop standards for static pressures above 200 GPa.

D. The ruby scale

There have been a number of publications proposing ruby scales, as reviewed in Sec. II. All of these have had some problems that are considered objectionable for a fundamental experimental calibration standard. MBSS78, BXM86, and MXB86 did not use quasihydrostatic media;

DO03 is an extension of MXB86 or is nonhydrostatic. AGZS87 is based on theoretical expectations for the extrapolation of the diamond EOS as is KLS03 and HO3. DLM04 had high-quality data in a quasihydrostatic medium, but did not select the most accurate SWRI for aluminum for their proposed calibration; the SWRIs used did not have the strength correction that we have implemented. In this paper we have presented a ruby scale. We have selected the best available existing data that meet the criterion of being measured in a quasihydrostatic medium, base the calibration mainly on SWRIs of metals with small thermal corrections, and include corrections to the Hugoniot data for material strength. This provides the most rigorous calibration of the ruby scale available at 150 GPa.

ACKNOWLEDGMENTS

Most of our experimental work was carried out at CHESS; we thank C.-S. Zha for his exceptional help at this facility and Arthur Ruoff for the use of some optical apparatus. We also thank David Mao for providing us with some of his beam time at NSLS when CHESS was down and Jingxhu Hu for her assistance. Sandeep Rekhi, Eran Sterer, and Christian Barthel are thanked for assistance with this work. This research was supported by the NSF, Grant Nos. DMR-9971326 and DMR-007182, and the US Army Missile Command.

- ¹A. Dewaele, P. Loubeyre, and M. Mezouar, *Phys. Rev. B* **70**, 094112 (2004).
- ²C.-S. Zha, H. K. Mao, and R. J. Hemley, *Proc. Natl. Acad. Sci. U.S.A.* **97**, 13494 (2000).
- ³A. Chijioke, W. J. Nellis, and I. F. Silvera, *J. Appl. Phys.* **98**, 073526 (2005).
- ⁴H. K. Mao, J. Xu, and P. M. Bell, *J. Geophys. Res.* **91**, 4673 (1986).
- ⁵G. J. Piermarini, S. Block, J. D. Barnett, and R. A. Forman, *J. Appl. Phys.* **46**, 2774 (1975).
- ⁶D. L. Decker, *J. Appl. Phys.* **42**, 3239 (1971).
- ⁷H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).
- ⁸O. Grasset, *High Press. Res.* **21**, 139 (2001).
- ⁹J. H. Eggert, K. A. Goettel, and I. F. Silvera, *Appl. Phys. Lett.* **53**, 2489 (1988).
- ¹⁰N. H. Chen and I. F. Silvera, *Rev. Sci. Instrum.* **67**, 4275 (1996).
- ¹¹C. Narayana, H. Luo, J. Orloff, and A. L. Ruoff, *Nature (London)* **393**, 46 (1998).
- ¹²P. Loubeyre, F. Occelli, and R. LeToullec, *Nature (London)* **416**, 613 (2002).
- ¹³A. Ruoff (private communication).
- ¹⁴L. Sun, A. L. Ruoff, and G. Stupian, *Appl. Phys. Lett.* **86**, 014103 (2005).
- ¹⁵R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, *Science* **176**, 284 (1972).
- ¹⁶K. Asuami and A. L. Ruoff, *Phys. Rev. B* **33**, 5633 (1986).
- ¹⁷H. Cynn, C. S. Yoo, B. Baer, V. Iota-Herbei, A. K. McMahan, M. Nicol, and S. Carlson, *Phys. Rev. Lett.* **86**, 4552 (2001).
- ¹⁸A. L. Ruoff and L. C. Chhabildas, *J. Appl. Phys.* **47**, 4182 (1976).
- ¹⁹J. M. Brown, *J. Appl. Phys.* **86**, 5801 (1999).
- ²⁰P. M. Bell, J. A. Xu, and H. K. Mao, in *Shock Waves in Condensed Matter*, edited by Y. M. Gupta (Plenum, New York, 1986), p. 125.
- ²¹D. L. Heinz and R. Jeanloz, *J. Appl. Phys.* **55**, 885 (1984).
- ²²H. Boppart, J. van Straaten, and I. F. Silvera, *Phys. Rev. B* **32**, 1423 (1985).
- ²³R. J. Hemley, C. S. Zha, A. P. Jephcoat, H. K. Mao, L. W. Finger, and D. E. Cox, *Phys. Rev. B* **39**, 11820 (1989).
- ²⁴I. V. Aleksandrov, A. F. Goncharov, A. N. Zisman, and S. M. Stishov, *Sov. Phys. JETP* **66**, 384 (1987).
- ²⁵H. J. McSkimin and P. Andreatch, *J. Appl. Phys.* **43**, 2944 (1972).

- ²⁶W. B. Holzapfel, J. Appl. Phys. **93**, 1813 (2003).
- ²⁷F. Occelli, P. Loubeyre, and R. LeToullec, Nat. Mater. **2**, 151 (2003).
- ²⁸K. Kunc, I. Loa, and K. Syassen, Phys. Rev. B **68**, 094107 (2003).
- ²⁹P. I. Dorogokupets and A. R. Oganov, Dokl. Akad. Nauk **391**, 515 (2003) [Doklady Earth Sci. **391A**, 854 (2003)].
- ³⁰A. Dewaele (private communication).
- ³¹Y. Wang, R. Ahuja, and B. Johansson, J. Appl. Phys. **92**, 6616 (2002).
- ³²P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, J. Phys. C **19**, L467 (1986).
- ³³A. C. Mitchell and W. J. Nellis, J. Appl. Phys. **52**, 3363 (1981).
- ³⁴R. G. McQueen, J. N. Fritz, and C. E. Morris, in *Shock Waves in Condensed Matter 1983*, edited by J. R. Asay, R. A. Graham, and G. K. Straub (Elsevier, Amsterdam, 1984), pp. 95–98.
- ³⁵H. E. Lorenzana, I. F. Silvera, and K. A. Goettel, Phys. Rev. Lett. **63**, 2080 (1989).
- ³⁶W. J. Nellis, J. A. Moriarty, A. C. Mitchell, M. Ross, R. G. Dandrea, N. W. Ashcroft, N. C. Holmes, and G. R. Gathers, Phys. Rev. Lett. **60**, 1414 (1988).
- ³⁷R. C. Powell and B. DiBartolo, Phys. Status Solidi A **10**, 315 (1972).
- ³⁸J. H. Eggert, F. Moshary, W. J. Evans, K. A. Goettel, and I. F. Silvera, Phys. Rev. B **44**, 7202 (1991).
- ³⁹D. M. Adams, R. Appleby, and S. K. Sharma, J. Phys. E **9**, 1140 (1976).
- ⁴⁰R. A. Noack and W. B. Holzapfel, in *Calibration of the Ruby-Pressure-Scale at Low Temperatures*, Boulder, CO, 1977 (Plenum, New York, 1978), p. 748.
- ⁴¹I. F. Silvera and R. J. Wijngaarden, Rev. Sci. Instrum. **56**, 121 (1985).
- ⁴²M. Chai and J. M. Brown, Geophys. Res. Lett. **23**, 3539 (1996).
- ⁴³L. C. Chhabildas and J. R. Asay, in *Shock-Wave and High-Strain-Rate Phenomena in Materials*, edited by M. A. Meyers, L. E. Murr, and K. P. Staudhammer (Marcel Dekker, New York, 1992), pp. 947–955.
- ⁴⁴B. F. Rozsnyai, J. R. Albritton, D. A. Young, and V. N. Sonnad, Phys. Lett. A **291**, 226 (2001).