Pressure calibration of diamond anvil Raman gauge to 310 GPa

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In order to develop an optical method for pressure determination in the multimegabar region, the first-order Raman spectra of diamond anvils were investigated at pressures up to 310 GPa. The high-frequency edge of the Raman band, which corresponds to the Raman shift of the anvil culet due to the normal stress, was calibrated against the sample pressure derived from the equation of state of Pt. The obtained pressure dependence of the edge frequency demonstrates the reliability of this diamond anvil Raman gauge. Up to the maximum pressure of this study, the relation between Raman frequency and normal stress at the diamond anvil culet is formally similar to the equation of state of a hydrostatically compressed isotropic elastic body having a bulk modulus of K_0 =547(11) GPa and a pressure derivative of the bulk modulus K_0'=3.75(20). © *2006 American Institute of Physics*. [DOI: 10.1063/1.2335683]

I. INTRODUCTION

Recently, it has been suggested that the first-order Raman mode of diamond anvils used in a diamond anvil cell (DAC) can be used as a laboratory-based pressure gauge in the multimegabar pressure range.[1–5] For the customary pressure determination method based on the equations of state (EOSs) of elemental metals, such as Pt, Au, or Ag, an x-ray diffraction experiment using a synchrotron radiation source is necessary.[7,8] On the other hand, the widespread ruby fluorescence method[9,10] is often inapplicable at pressures higher than 100–150 GPa, due to weakening of the fluorescence signal and/or due to the nonhydrostatic pressure effects. Therefore, a conventional method for the pressure determination in this high-pressure region is desired.

The method for determining pressure using Raman spectroscopy of diamond anvils, the so-called diamond anvil Raman method, was proposed by Hanfland and Syassen.[1] They found that the high-frequency edge of the Raman band was correlated with the normal stress at the culet face and the edge frequency had a linear dependence on the pressure in the sample chamber up to 30 GPa. In our recent studies of the Raman spectra of diamond anvils, the high-frequency edge was calibrated against the EOS scale of Pt up to 250 GPa (Ref. 5) and was found to be a unique function of pressure in the sample chamber, being almost independent of loading conditions such as the size of the anvil culet, the pressure medium or sample, and the gasket material. Up until now, Vohra *et al.*,[2] Eremets,[3] Popov,[4] and Sun *et al.*[6] have also proposed pressure calibration curves and discussed the usefulness and reliability of the Raman method. This method has already been used in an optical study of hydrogen[11] and a structural study of scandium[12,13] above 200 GPa.

However, the investigation of the Raman scattering in diamond anvils in the multimegabar range has been limited to a few reports. For reliable pressure determination by this method, further experiments to confirm the universality of the calibration curve are needed. In this study, the pressure calibration is extended up to 310 GPa and a universal calibration curve is proposed.

II. EXPERIMENT

Two pressure-generation experimental runs using a DAC were performed with a gasketed high-pressure technique. In the first experimental run, using diamond anvils with a culet diameter of 35 μm, the maximum pressure was 297 GPa. The second run with a culet diameter of 30 μm reached 333 GPa, while the diamond broke at the highest pressure soon after laser irradiation. The load axis of the diamond anvils was fixed to the [100] crystal direction. Re metal was used as the gasket and no pressure transmitting medium was used. In this study, low-luminescence type Ia diamonds were used for the anvil, because the luminescence from the diamond anvil rapidly increased as the pressure was increased above 200 GPa and it was often difficult to detect the scattered light from the anvil culet.

High-pressure Raman scattering experiments were carried out using the micro-optical system of the JASCO model NR-1800 spectrometer. Its resolution was within ± 1 cm^{-1}. Details have been described in a previous report.[5,14] The 632.8 nm line from a He–Ne laser with a power of 35 mW was used for excitation. The Raman spectra were collected with a backscatter configuration using a charge-coupled device (CCD) detector. The laser beam was focused on the center of the interface between the anvil culet and the sample chamber because the pressure distribution at the culet center is almost flat.[5]

Pressure was determined using the EOS of a Pt pressure marker[15] embedded in the sample chamber. In order to determine the volume of the pressure standard precisely, powder x-ray diffraction experiments were carried out at 300 K by an angle-dispersive method with an image plate detector and the monochromatic x rays (λ=0.4966 Å) of the synchrotron radiation (SR) source on BL10XU at SPring-8. Experimental details are described elsewhere.[7,8] The uncertainty in

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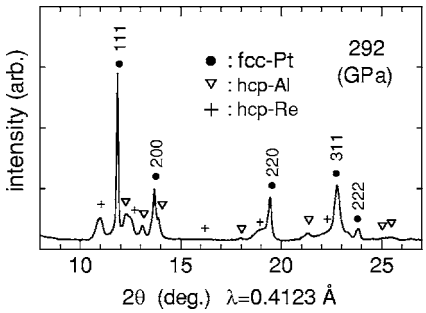

FIG. 1. Typical diffraction pattern of the Pt pressure marker collected at pressure in the multimegabar range using diamond anvils with a culet diameter of 30 μm. The estimated pressure was 292(3) GPa. The d values are listed in Table I.

the pressure measurement in the multimegabar range was estimated to be within 8 GPa from the pressure distribution in the sample chamber and the error in the lattice parameter of the Pt marker. The pressure distribution in the sample was estimated to be ~5 GPa around 200 GPa from the line broadening of the diffraction peaks of the Pt marker. The error in the average pressure, which was estimated from the standard deviation of the lattice constant of Pt, was within ±2 GPa below 250 GPa, while this increased to ±3 GPa at 310 GPa. This error was due to the deviatoric stress effect of the pressure marker. A typical diffraction pattern and d-value data of the Pt marker at 292 GPa have been shown in Fig. 1 and Table I, respectively.

III. RESULTS

Typical Raman spectra from the culet center of loaded diamond anvils are shown in Fig. 2(a). The first-order Raman band of a diamond is located at $\nu_0=1333\pm1$ cm^{-1} at normal pressure and exhibits a blueshift with applied stress. In the case of a diamond anvil under applied load, the Raman band undergoes a significant broadening as shown in the figure. The spectra reflect the stress states of the anvil from the unstressed table face to the highest stressed culet face due to the low spatial resolution of the present optical system to the axial direction. As a result, the spectra are characterized by the steep edges at the high- and low-frequency sides, which come from the spectra of the culet and the table faces of the anvil, respectively. The triply generate first-order Raman band of a diamond is split into a singlet and a doublet band

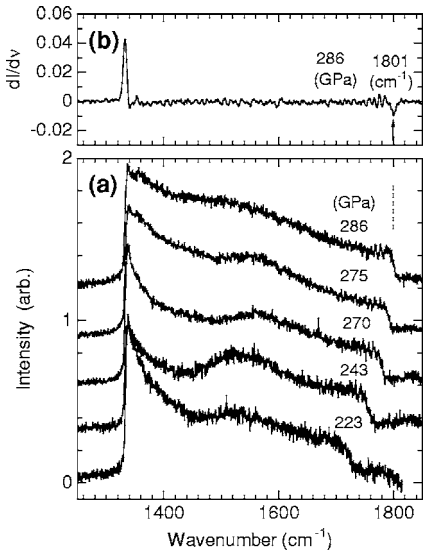

FIG. 2. (a) Typical Raman spectra from the center of the diamond anvil culet at various pressures in the multimegabar range and (b) the differential spectrum, $dI/d\nu$ at 286 GPa. The high-frequency edge of the Raman band was defined as a minimum of the $dI/d\nu$.

due to a uniaxial stress. Therefore, strictly speaking, the high-frequency edge comes from the singlet mode with a larger frequency shift.[1]

The high-frequency edge is often different in shape depending on the pressure conditions and/or the configuration of the optical system as previously reported.[1–6] Therefore, the definition of the edge frequency without any arbitrariness is needed for a reliable determination of the pressure. In this work, the high-frequency edge was defined as the minimum of the differential spectrum, $dI/d\nu$, as shown in Fig. 2(b). The accuracy of the edge frequency determined by this method is within ±2 cm^{-1}. The obtained value of the frequency at each pressure is summarized in Table II.

Figure 3 shows the pressure dependence of the edge frequency together with previous results.[5] The present data link continuously to our previous data and show a clear correlation to the sample pressure. The correlation is unique and almost independent of the loading conditions such as the culet size and the sample material. Comparing our results with previous results, the data by Popov[4] show good agreement with ours, while other data seem to slip to the higher pressure side compared to our data. As mentioned above, the most important things are the definition of the edge fre-

TABLE I. The d values of the Pt pressure marker of the x-ray diffraction pattern at 292 GPa shown in Fig. 1.

fcc-Pt	$P=292(3)$ GPa $a=3.4538(23)$ Å, $V=41.202(66)$ Å^3		
$h\ k\ l$	d_{obs} (Å)	d_{cal} (Å)	Error (Å)
1 1 1	1.994 90	1.994 09	0.000 81
2 0 0	1.728 74	1.726 94	0.001 80
2 2 0	1.219 81	1.221 13	−0.001 32
3 1 1	1.041 66	1.041 38	0.000 28
2 2 2	0.997 16	0.997 05	0.000 11

TABLE II. Observed Raman frequency at the diamond anvil culet under various pressure conditions.

P (GPa)	ν (cm^{-1})	Scale	Sample	Culet diameter (μm)
223	1724	Pt	Sc	35
243	1756	Pt	Sc	35
270	1781	Pt	Sc	35
275	1791	Pt	Sc	35
286	1801	Pt	Sc	35
286	1803	Pt	Sc	35
290	1807	Pt	Sc	35
297	1811	Pt	Sc	35
292	1802	Pt	Al	30
310	1824	Pt	Al	30

quency and the pressure scale. The definition and/or the scale in these previous studies are different from those of the present study or are not clear. This would cause the discrepancy.

IV. PRESSURE-EDGE FREQUENCY RELATIONSHIP

Aleksandrov *et al.*[16] reported that pressure P is expressed as a quadratic function of relative density $\Delta\rho/\rho_0$ in the case of diamond for the quasihydrostatic pressure $P \leqslant 100$ GPa:

$$P(\rho) = K_0 \frac{\Delta\rho}{\rho_0}\left[1 + \frac{1}{2}(K_0' - 1)\frac{\Delta\rho}{\rho_0}\right], \tag{1}$$

where K_0 is a bulk modulus and K_0' is its pressure derivative. Recent EOS and phonon calculations by first-principle methods have also reported that this expression fits the calculated results up to 600 GPa.[17] The volume dependence of phonon frequencies $\nu(V)$ is usually described as follows:

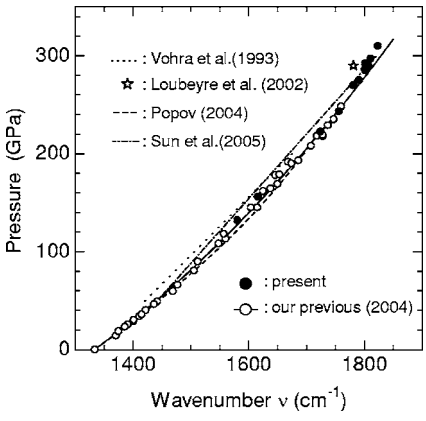

FIG. 3. The pressure dependence of the edge frequency together with previous data. The solid circles show the present data. The open circles and the solid line correspond to our previous data (Ref. 5). The dotted line, broken line, and single dotted broken line correspond to the calibration curves proposed by Vohra *et al.* (Ref. 2), Popov (Ref. 4), and Sun *et al.* (Ref. 6), respectively. A star shows the data by Loubeyre *et al.* (Ref. 11). The errors in the pressure measurement and the edge frequency of the present data are within 8 GPa and 2 cm^{-1}, respectively.

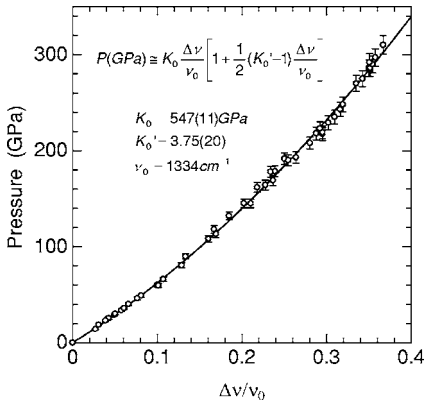

FIG. 4. The pressure vs the relative edge frequency $\Delta\nu/\nu_0$ relationship. The solid curve shows the least-squares fit to our present and previous data using a quadratic function. The error bars represent an uncertainty of 3% for pressure values.

$$\frac{\nu(V)}{\nu_0} = \left(\frac{V}{V_0}\right)^{-\gamma} = \left(\frac{\rho}{\rho_0}\right)^{\gamma}, \tag{2}$$

if we assume that the mode Gruneisen parameter $\gamma = -d\ln\nu/d\ln V$ is independent of volume V. Considering the fact that the value of γ nearly equals 1, $\Delta\nu/\nu_0 \cong \Delta\rho/\rho_0$. So, Eq. (1) can be reformulated to relate hydrostatic pressure in diamond to the relative Raman frequency change $\Delta\nu/\nu_0$:

$$P(\mathrm{GPa}) \cong K_0 \frac{\Delta\nu}{\nu_0}\left[1 + \frac{1}{2}(K_0' - 1)\frac{\Delta\nu}{\nu_0}\right]. \tag{3}$$

Using the analytical form of Eq. (3) with the edge frequency $\nu_0 = 1334$ cm^{-1} at ambient pressure, our present and previous experimental data of pressure versus the edge frequency were fitted by the least-squares method. The fitted function is shown in Fig. 4. If an uncertainty of 3% is assigned to pressure values, a satisfactory fit (in terms of the variance) was obtained. This pressure uncertainty is reasonable considering the experimental error of pressure. The obtained values for the linear and nonlinear coefficients K_0 and K_0' in Eq. (3) were 547(11) GPa and 3.75(20), respectively. Up to the maximum pressure of this study, the relation between Raman frequency and normal stress at the diamond anvil culet is formally similar to the equation of state of a hydrostatically compressed isotropic elastic body having a bulk modulus of $K_0 = 547(11)$ GPa and a pressure derivative of the bulk modulus $K_0' = 3.75(20)$. For comparison, the equation of state parameters of diamond under hydrostatic pressure are $K_0 = 445 \pm 20$ GPa and $K_0' = 3.5 \pm 0.5$.[17]

The universality of the relationship between the sample pressure and the edge frequency was confirmed in this study. The pressure shift of the edge frequency reflects the stress state at the culet of the anvil under the uniaxial stress. Recently, we have investigated the stress state of the culet of a loaded diamond anvil with the loading axis in the [111] crystal direction.[18] The shear stress at the culet center of the working diamond anvils has been estimated as a function of the generating pressure up to multimegabar pressure. According to that result, the value of the shear stress in the multimegabar range was sufficiently small compared with the shear strength of diamond.[19] This means that diamond

anvils work within the elastic limit of diamond. Therefore, the universal correlation results from the elastic response of the culet face of the diamond anvil to the normal stress as discussed from recent finite-element calculations.[20]

V. CONCLUSION

We measured the high-frequency edge of the first-order Raman band of the diamond anvil as a function of the sample pressure up to 310 GPa. A universal relationship between the edge frequency and the pressure was confirmed and a calibration curve in the multimegabar pressure was proposed. Our results demonstrate the usefulness of the pressure measurement based on diamond anvil Raman spectra.

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