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Megabar high-pressure cells for Raman measurements

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Experimental aspects of Raman measurements at megabar pressures are considered. Features of diamond anvil cells working above 200 GPa are described. Problems of luminescence background at megabar pressures and the use of low-luminescence diamonds are considered. Methods of pressure measurements at very high pressures are discussed. The pressure dependence of the Raman shift from the diamond anvil tip was used as a reliable estimate of the pressure. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: megabar pressures; diamond; pressure scale

INTRODUCTION

This paper is an update of an earlier review,[1] concentrating on features of the Raman scattering experiment at megabar pressures. This experimental approach can also be useful for measurements at lower pressures.

EXPERIMENTAL

Diamond anvil cell

Achievement of pressures above 200 GPa inevitably needs a decrease in the size of the diamond anvil culet down to 20–50 μm. With such small culets, alignment (tilting) of anvils to make them parallel to each other becomes practically impossible. Instead, culets are cut precisely parallel to tables of the anvils. In addition, tungsten carbide supports are placed precisely perpendicular to the axis of the cell. Thus the anvils placed on supports are exactly parallel to each other and alignment of the anvils comes down to translation. In the first step, the center of one of the culets is placed at the axis of the diamond anvil cell (DAC) (the proper position can be controlled by rotation of the piston of the DAC). Then another culet is matched by translation of the anvil with accuracy better than a few micrometers. Any direct touching of culets should be avoided. Construction of the DAC has to be robust. In particular, the piston-cylinder guide should be well honed and have no play. Figure 1 shows our very simple non-magnetic cell which regularly works up to 260 GPa at temperatures down to the millikelvin range in high magnetic fields of up to 18 T.[2]

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Luminescence from diamond anvils

A typical problem at megabar measurements is the enhanced luminescence background which obscures the Raman spectrum. Often strong luminescence appears at pressures above ~150 GPa. The origin of this luminescence is not well understood. It appears that it is driven by large uniaxial stresses in the diamond tip. These stresses can activate impurities by reduction of local symmetry and changing of selection rules and the scheme of transitions. High luminescence also can be caused by defects created by high shear stresses. Maximum shear stresses concentrate beneath the culet at depths of the order of magnitude of the diameter of the culet (~60 μm for a 20 μm culet[3]).

Luminescence from this area is the most probable. In one experiment, we clearly observed the origin of the enhanced luminescence which appeared above 120 GPa. It was localized at the axis of the cell therefore it seemed to originate from the sample. However, on releasing the pressure, cracks developed beneath the center of the diamond tip while the luminescence spectrum remained the same after extracting the sample.

This and many other experiments indicate that defects are created in the highly stressed region.[4] Laser illumination of this volume can induce a catastrophic growth of defects (cracks). This picture can explain the well-established fact that diamonds often break at the highest pressures soon after laser illumination. Short-wavelength radiation (blue light) is especially dangerous. This light is highly absorbed also because of closing of the diamond gap at high uniaxial stresses.[5,6] In our experience, a power of ~10 mW can cause failure of the anvil at pressures above 150 GPa. Therefore, at higher pressures, excitation with blue laser radiation is potentially dangerous. Red Kr^+ or Ti–sapphire lasers become the most suitable sources for studies in the megabar range. In our experience, diamonds do not break even when

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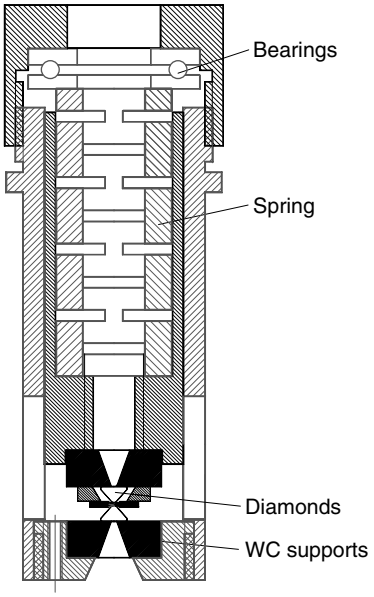

Figure 1. Clamped megabar diamond anvil cell made of non-magnetic NiCrAl alloy.

several hundred milliwatts of red light are used. Further, luminescence is usually significantly diminished under red light excitation.

Low-luminescence diamonds

The most efficient way of eliminating the luminescence is to use synthetic type IIa diamonds. These diamonds have very reproducible properties from stone to stone and have a very low nitrogen content in the 0.01–0.1 ppm range. They are also very pure with respect to other impurities and defects. Even isotopically pure diamonds can be grown.[7] As a result, luminescence from synthetic diamonds is very low (Fig. 2), an order of magnitude lower than for natural stones. With these anvils, very weak Raman scattering can be measured with large accumulation times. They show low luminescence up to pressures of 270 GPa.[8] Synthetic IIa diamonds have excellent mechanical properties,[9,10] and have been used to generate very high pressures of 370 GPa.[7,8] Synthetic diamonds are still rare commercially, but are available from Sumitomo Electric and the Technological Institute for Superhard and Novel Carbon Materials (Troitsk, Moscow region, Russia).

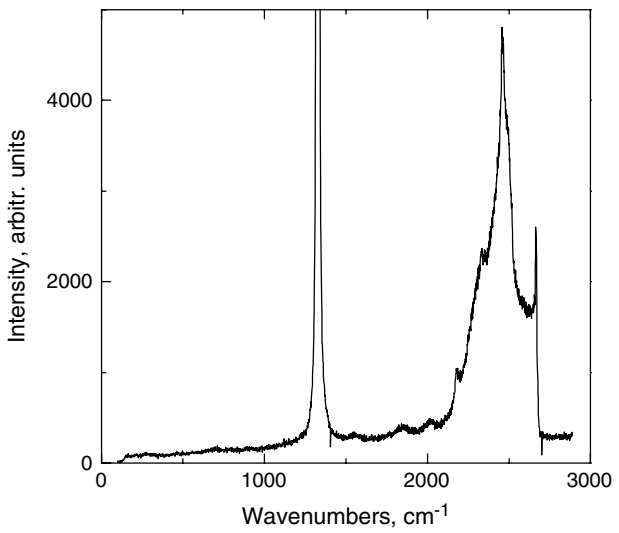

Figure 2. Typical Raman spectrum from synthetic diamond anvil.

RESULTS

Pressure measurements

Measurement of pressure in DACs at megabar pressures is a difficult problem. First, the present calibration of the ruby gauge is based mainly on the early work of Mao *et al*.[11] In that work, the ruby luminescence shift was calibrated up to 80 GPa against the equation of state of some metals known from shock-wave data. This scale coincides with a primary pressure scale built from Brillouin data on MgO up to 55 GPa.[12] The ruby scale should be checked at pressures above 100 GPa. In spite of the uncertainty of the accuracy of pressure determination, the ruby gauge remains the most important pressure calibrant. At pressures above 150–200 GPa, the spectra of ruby change: in addition to the known R_1 and R_2 peaks, other bands arise,[13] which makes the identification of the R_1 peak complicated (Fig. 3). For reliable determination of pressure, all peaks of the spectrum should be taken into consideration. Another problem is the drastic weakening of the signal. Therefore, the ruby signal is easily masked by background luminescence. A very effective

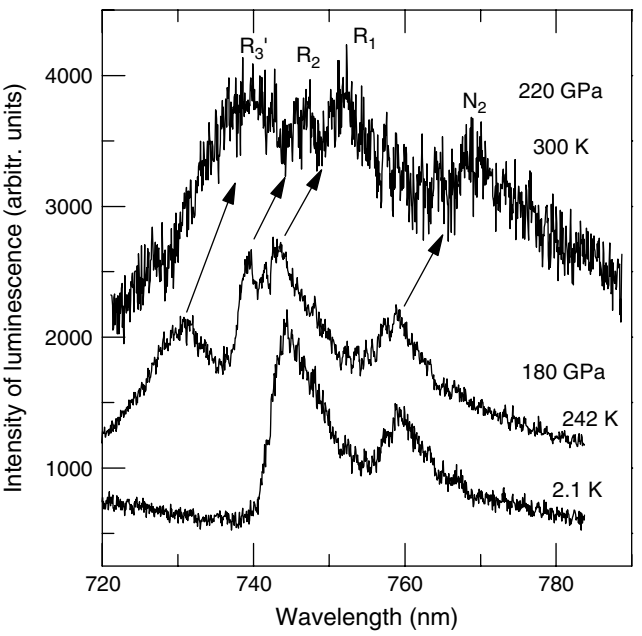

Figure 3. Spectra of ruby luminescence at high pressures and low temperatures.

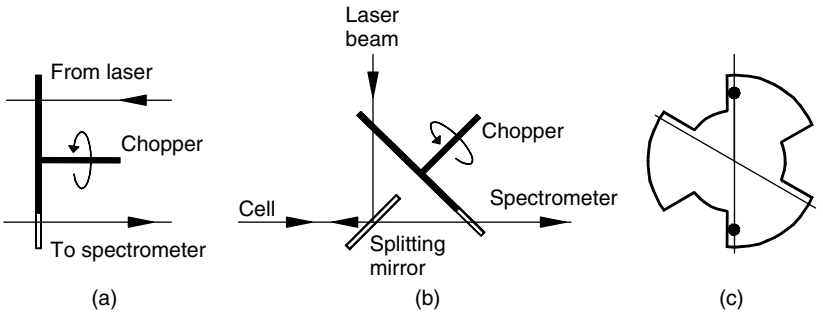

Figure 4. Optical scheme for measurement of luminescence of ruby. (a) Position of the chopper disk for measurement of ruby luminescence with elimination of diamond fluorescence (luminescence light passes to the spectrometer when the laser radiation is blocked). (b) One of the practical schemes of positioning of the chopper disk. (c) Chopper disk: stop radiation blades are wider than openings for approximate diameters of laser and ruby luminescence beams.

method of rejection of the diamond luminescence is the chopper technique.[13,14] This method is based on the large difference in the lifetimes of luminescence from diamond (nanoseconds) and ruby (milliseconds): the detector is open only when the laser is blocked. We found the simplest method for measurements: instead of two synchronized choppers, we used only one but placed properly in the optical scheme (Fig. 4). This is the simplest rotating blade and no regulation or synchronization of the motor is needed. This chopper can be made 30 min at negligible cost (any motor and blade cut from a carton or aluminum sheet) and works amazingly effectively.

As mentioned above, red light excitation is preferable for Raman studies at megabar pressures. Fortunately, this does not make serious difficulties for ruby measurements. Ruby can be pumped with a laser of wavelength close to the R_1 line.[15] We found that ruby luminescence can be excited even when the pump energy is lower than the R_1 energy (Fig. 5). The maximum signal can be achieved by tuning the energy of a Ti–sapphire laser.

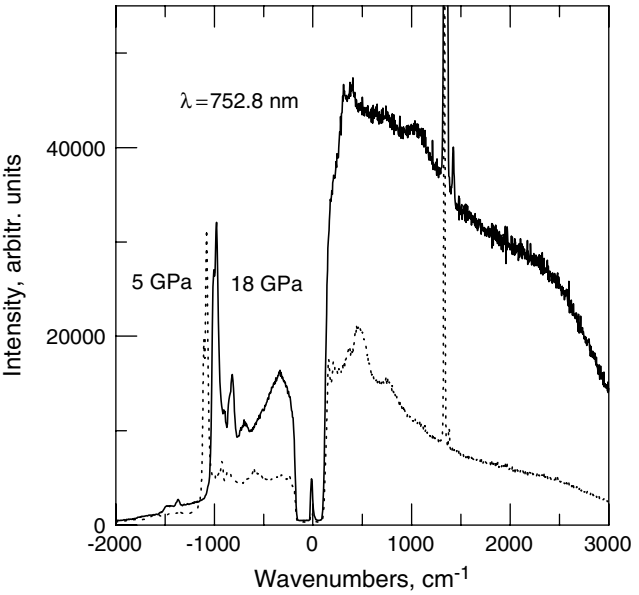

Figure 5. Raman spectrum from sodium azide sample together with the first-order Raman peak from diamond anvil. Ruby luminescence spectra are seen at energies lower than the excitation line.

Diamond anvil scale

Because of some of the disadvantages of the ruby gauge, other materials are sought as suitable pressure calibrants. One of the simplest ways to use a single Raman line from diamond. At ambient pressure the Raman signal from the diamond sample is not visible over the background of the diamond anvils. However, this peak shifts with pressure faster than the Raman band from the anvils.[16] At ~10 GPa it appears out of the diamond anvil background. Its shift was monitored under hydrostatic conditions up to 140 GPa.[17] At present, this scale has not yet been developed for practical application. There are difficulties with the preparation and placing of diamond samples of thickness in the micrometer range in the cell, and the signal from the thin samples is low.

It is very attractive to use the Raman shift from a diamond anvil for pressure determination: the strong band from diamond anvils always accompanies the signal from the sample [Fig. 6(a)]. In this case the anvil itself is the pressure gauge. This approach was first proposed by Hanfland and Syassen,[16] where careful analysis of Raman spectra from the stressed anvils was done at pressures up to 30 GPa. Principally, this calibration can be done because stresses in the anvil (and measured Raman shift) are determined by the pressure distribution over the anvil. The question is how universal this calibration could be: it should not depend strongly on the geometry of the anvil, gasket and so on. At the first glance, this is doubtful, because the picture of stresses in the tip of the anvil is complicated and depends on many parameters.[3,18,19] However, at some points of symmetry stresses are well understood. The simplest area is the center of the culet. Here there is a large uniaxial component along the z-axis: $\sigma_r/\sigma_z \approx 0.5$ according to calculations,[3,18] where σ_r is the radial stress and σ_z is the vertical stress which

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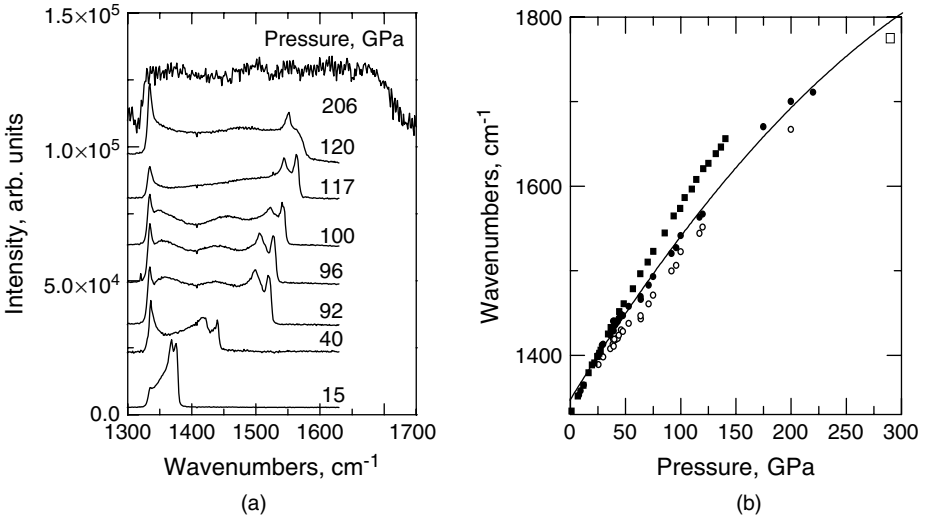

Figure 6. (a) Raman spectra from tip of diamond anvil. (b) Pressure dependence of the peaks of the Raman band taken from tip of diamond anvils shown in (a). The solid line is a polynomial fit of the high-frequency peak. One point (open square) was taken from Ref. 21; dashed line and other square points are data from Ref. 17: pressure dependence of Raman peak measured from a sample of diamond under quasi-hydrostatic conditions of helium medium.

equals the pressure in the sample at the surface of the anvil. This ratio is approximately valid in many cases. As follows from the theory of elasticity, local tensors of stresses at the loaded surface depend strongly on the particular local pressure distribution at a given point, and are not sensitive to remote areas.[20] In particular, at the center of the culet the pressure distribution typically is nearly flat. This means that the ratio between the main stress components should be approximately the same for anvils of different forms, if only the probed region is smaller than the size of the flat pressure distribution area. This suggestion should be checked by the study of anvils of different shapes and various gaskets. We did not do this systematically, but probed different anvils of 50–300 μm diameter culet and bevelled angles of 0–12°. Data from different runs lay well on the same plot [Fig. 6(b)].

Some precautions should be taken for correct measurements. The main point is that the measured probed volume should be as small as possible (a few micrometers for megabar cells) and taken from the volume adjacent to the center of the culet. An area of a few micrometers is easily selected with a field stop. We also found that the signal decreases dramatically on moving of the laser focus from the surface of the diamond culet into the sample. This means that a volume of a few micrometers depth is probed also along the axis of the anvil. We believe that the measured dependence of the Raman shift from the diamond anvil (Fig. 6) can be used for the reliable estimation of pressure.

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