Review Article

Raman Spectroscopy at High Pressures

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Raman spectroscopy is one of the most informative probes for studies of material properties under extreme conditions of high pressure. The Raman techniques have become more versatile over the last decades as a new generation of optical filters and multichannel detectors become available. Here, recent progress in the Raman techniques for high-pressure research and its applications in numerous scientific disciplines including physics and chemistry of materials under extremes, earth and planetary science, new materials synthesis, and high-pressure metrology will be discussed.

1. Introduction

Raman spectroscopy probes elementary excitations in materials by utilizing inelastic scattering processes of a near ultraviolet, visible, and near infrared monochromatic light source (commonly a laser). The scattered radiation forms a spectrum near that of the excitation laser wavelength. The results are easily accessible for recording as very sensitive detectors are available in this spectral range.

The main strength of the Raman spectroscopy is the ability to provide a great wealth of easily analyzable information very rapidly. The Raman spectra can be used to characterize the elastic, vibrational, electronic, and magnetic subsystems through the observations of the corresponding elementary excitations. The Raman spectra of phonons (lattice and molecular vibrations) have a very high selectivity, thus permitting finger-printing analysis of the materials phase that can include its composition and state. The information about the crystal structure is provided through the vibrational selection rules, which govern the Raman activity of phonon modes depending on their symmetry and the wave vector. The access to electronic and magnetic states is attained through the coupling to the vibrational states, and through the observations of the spectra of the electronic and magnetic excitations.

As the spectra of elemental excitation change with the application of pressure, the associated phenomena can be

effectively studied by *in situ* Raman spectroscopy. These include changes in the energy of the vibrational excitations, phase transformations (including melting), chemical reactivity, and magnetic and electronic transitions. This information can be used for multiple applications because these transformations are of interest for fundamental physics and chemistry, materials, and earth and planetary science. Last (but not least), Raman spectroscopy is a great tool for measurements of pressure at both extremely low and extremely high temperatures.

Previous comprehensive reviews on Raman spectroscopy at high pressures [1–3] have mainly discussed mineralogical and environmental applications. Other reviews [4–6] need updating for recently developed techniques and newly obtained groundbreaking experimental results, which often created new scientific understanding. Moreover, a field of high-pressure high-temperature Raman studies using laser heating in diamond anvil cells (DACs) has only recently become mature. All this made a new review paper desirable. Here, the author presents a review of Raman spectroscopy methods and applications at high pressures, which include these new developments.

2. Development of Raman Techniques

In high-pressure Raman instrumentation, special care must be taken to interface the technique with the DAC. The

typical samples dimensions in the DAC are several tens of micrometers and a few micrometers in thickness; these dimensions are even smaller if measurements to ultrahigh pressures (>100 GPa) are planned. The presence of an optically thick diamond window (≥ 2 mm) in the optical path causes large geometric and chromatic aberrations, which affect the image quality, the signal collection efficiency, and the depth selectivity. Until recently the use of optics with a large numerical aperture was not feasible because it conflicts with the requirements of stability of diamond anvils and supporting backing plates. Objective lenses with a large working distance (normally ≥ 10 mm) are also necessary. Moreover, diamond windows in the optical path produce parasitic back reflections, which make Raman measurements at low frequencies difficult. This is because the specularly reflected and elastically scattered laser light increases the background level thereby decreasing the signal-to-noise ratio. Also, diamond anvils fluorescence in the laser beam also contributes to the background level. All these factors call for the custom-made laser microscopes to interface the DAC as the commercial microscopes typically do not provide a sufficient level of flexibility to address all the issues described above.

The custom Raman microscope for DAC has been described in our previous publications [5–7] (Figure 1). Here the author will focus on the presence of the intermediate field aperture (spatial filter) to reduce the spurious background, the ability to easily change the excitation wavelength (as this helps to provide the optimum excitations conditions and to decrease the fluorescence), and the flexibility in choosing the scattering geometry.

A confocal field aperture with a diameter corresponding to the dimension of the laser spot attenuates the spurious elastically scattered laser radiation substantially. Moreover, it makes the depth of focus smaller thus cutting substantially the fluorescence background from the diamonds. Although the intermediate field apertures are redundant in the sense that the confocal geometry can be realized using the entrance slit of the spectrometer and by narrowing the detector readout in the nonspectral direction [8], the latter strategy is insufficient for the DAC operation (based on our experience) because of a substantially increased level of the spurious radiation compared to that for free-standing samples.

The use of angular excitation geometry (Figure 1) allows a drastic reduction in background spurious radiation compared to pure backscattering geometry, thus increasing the signal-to-noise ratio and making easier the access to the low-frequency spectra. Moreover, this technique allows reducing substantially Raman and fluorescence background signals from the diamond anvils because the corresponding signals, excited mainly off axially, are suppressed more efficiently than in the case of the axial laser illumination (pure backscattering geometry). This will be illustrated later on examples of studies of metals and high-temperature superconductors. A conventional backscattering geometry can also be used for the system presented in Figure 1 by introducing a beamsplitter (neutral optical density or dichroic).

To realize the angular excitation geometry the DAC must be designed or modified to allow the angular light access. Previously, specially designed tungsten carbide seats with angular conical holes have been used for this purpose [5, 9]. To focus the laser radiation on the sample, one needs to use a separate lens (or an objective lens). Due to geometric considerations, this lens has longer focal length compared to that which collects the scattered radiation. This effectively increases the minimum laser spot dimension at the sample. In addition, use of angular laser incidence geometry results in further increase of the laser spot because as off-axis geometric aberrations (e.g., astigmatism) which affect the dimensions and the shape of the focused laser beam in this case. Both these factors place limits on the applicability of this geometry (e.g., for heterogeneous samples). Nevertheless, the use of the angular geometry was found to be crucial for obtaining high-quality spectra in the case of metals [5, 6, 10, 11].

Raman spectroscopy has improved substantially in its ability to perform rapid measurements due to the development of extremely sensitive and low-background array detectors (CCD), holographic transmission optics [12], and fast imaging spectrometers (e.g., [1, 13]). More recently, new hard-coated optical filters [14], which have comparable transition width of the transmission band to those manufactured using a holographic technology, have appeared on the market. Notch, bandpass, and dichroic filters/beamsplitters using this technology efficiently block undesirable Rayleigh-scattered light and obviate the need for cumbersome low-transmission double subtractive monochromator-filter systems for routine measurements above 50 cm^{-1} . Moreover, recently a new generation of notch and bandpass filters with a transition width as narrow as 10 cm^{-1} has been developed based on a solid-state technology [15]. These filters are expected to be much more environmentally stable, and show no degradation over time.

Application of Raman spectroscopy for studies at very high pressures often requires capability to perform a rapid change of the excitation wavelength. This is needed to determine the nature of the bands observed (e.g., Raman versus fluorescence), to provide the optimum excitation (e.g., for ruby fluorescence), and to study the resonance phenomena (e.g., [16]). Modern Raman spectrometers, which use the very light-efficient and narrow transition width filter technologies (see above), are less flexible for tuning of the excitation wavelength compared to conventional triple-stage spectrometers. Nevertheless, the micro-Raman system, which is described here (Figure 1) is capable for a rapid change in the excitation wavelength covering the spectral range up to 100 nm without the need to use another set of holographic filters. This is achieved by changing the angular positions of the filters with respect to the laser and the scattered beam directions. These rotations of the filters do not affect the system alignment.

One essential improvement in the Raman techniques for high pressure would be a confocal Raman imaging (e.g., in the DAC). Newly designed laterally supported diamond anvils [17] allow using objective lenses with much larger numerical aperture (e.g., $\text{NA} = 0.7$) than with the anvils

FIGURE 1: Layout of the Raman optical microscope system for diamond anvil cells. Double-side arrows designate moving parts (see text for explanations).

of conventional design. In principle, this makes 3D Raman mapping possible. A remaining obstacle is large optical aberrations introduced by diamond windows. These aberrations distort the wave front thus making the depth-selective measurements difficult. This problem can be solved using a specialized compensating optics; the work is currently in progress.

In situ Raman measurements in laser-heated DAC has been developed recently [18, 19]. Use of near IR lasers (1060 nm) as a heating source allows reducing the heating spot and producing more stable heating conditions compared to CO₂ laser heating used previously [20]. These advantages have become even more noticeable when near IR fiber lasers with the improved mode quality and stability became commercially available. This improved laser beam quality allows very local heating of the samples in the DAC cavity, thus opening a possibility to use the technique at very high pressures. Recently, the technique has been further improved by the development of laser beam shapers, which allow controlling the laser power distribution in a focal plane [21, 22]. The use of a flat top or bimodal power distribution makes the heating conditions more stable and reduces the radial temperature gradients.

Heating of materials, that do not absorb the laser radiation is challenging. A thin foil with a small hole(s) or powder made of chemically stable metals (e.g., Pt) can serve as a laser beam absorber (coupler) thereby producing high-temperature conditions for the surrounding sample material [18, 19]. Arguably the best results for the *in situ* Raman spectroscopy have been obtained when couplers with small holes have been used [18, 19]. The coupler is heated by an IR heating laser spot, which is larger than the hole, while Raman scattering of the material in the hole is excited by another tightly focused visible laser. This geometry decreases the temperature gradients through the probed material.

Furthermore, application of thermal insulation layers near the diamond anvil tips (which remain cool during the experiment owing to a very large thermal conductivity of diamond) eliminates the sample from these areas thereby further reducing the temperature gradients across the probed sample. A double-sided laser heating helps decreasing the temperature gradients across the sample contained in the coupler hole. The laser power can be split to two sides and controlled independently at each side using a system of polarization cubes and wave plates [22]. This system has been recently automated for data acquisition, which includes performing all the spectral measurements (Raman and radiative temperature measurements) at variable heating laser power [23]. This upgrade allows saving up to 90% time compared to manual data acquisition. This improvement is important for experiments with highly chemically reactive materials such as, for example, hydrogen [24].

The thermal radiation emitted by the sample and the coupler makes Raman measurements at high temperature challenging. One can avoid a substantial part of the thermal radiation by discriminating it spectrally and spatially. This can be achieved by using a blue excitation wavelength (e.g., 458 nm of a solid-state laser) and by using a confocal backscattering geometry. High-quality Raman spectra can be obtained up to approximately 2000 K in the experimental environment [19] (see also [25]). At higher temperatures, when thermal radiation rises above a critical threshold and obscures the Raman signal, a pulsed Raman system with 532 nm excitation synchronized with the gated intensified CCD detector can be used [26] (see also [27]) in combination with continuous [28] or pulsed laser heating [22]. As the detector collects the entire Raman signal (the Raman processes are very short, normally <1 ps) during the relatively short gate time and is closed between pulses, any continuous (or lasting longer) spurious radiation is suppressed by a

factor that is proportional to the ratio of the time interval between pulses to the gate width. The suppression factors up to 50000 have been reported [26] providing the possibility of acquiring Raman signals at temperatures exceeding 5000 K.

The advances in Raman instrumentation introduced above have enabled a number of new opportunities for the Raman studies at high pressures, which will be described below. Arguably, the most prominent achievement is the ability of the modern Raman systems to perform very rapid measurements (<1 s acquisition time) thus enabling experiments under extremely high pressures and temperatures (P - T).

3. Raman Studies at High Pressures

3.1. Phase Diagrams of Diatomic Molecules. Raman spectroscopy is ideally suited for studying the evolution of the bond character in diatomic molecules under compression because measurements of their vibrational properties provide a powerful diagnostic of this process. The electronic density function changes with compression to minimize the total energy of the system. For the molecular materials, pressure tends to destabilize the intramolecular bonds as the kinetic energy of the participating electrons increases steeply with compression (e.g., [29]). This process may be complicated by other phenomena such as, for example, the formation of some intermediate states [30, 31], which affect the molecular stability. Study of simple molecules such as diatomics is a valuable approach to solve this problem.

The behavior of hydrogen under pressure is of special interest because of the simplicity of the electronic structure and because of its dominant abundance in the universe, making it the major constituent of stars and planets. Today, Raman spectroscopy technique is still limited in pressure and temperature (to roughly below 150 GPa and 2000 K) making study of hydrogen under conditions of molecular dissociation very challenging. Therefore, the author will begin by reviewing the behavior of the halogens, which can be considered as analogous to hydrogen in electronic structure because hydrogen can be viewed as a group VII element [32], and the phenomena of interest in these materials occur at much lower pressures than in hydrogen (<100 GPa). Recently, iodine (I_2) and bromine (Br_2) have been extensively studied [33]. The application of Raman spectroscopy was crucial in revealing the bonding character change, the insulator-metal transition, and the presence of an intermediate charge modulated phase as a function of pressure [34]. Indeed, the Raman spectra revealed a number of changes with pressure, which can be associated with the observations obtained by other techniques, such as X-ray diffraction [34], X-ray absorption spectroscopy [35], and electrical conductivity [36]. Raman measurements show discontinuous frequency changes and the appearance of new bands that can be related to metallization. These observations could also be associated with an additional subtle phase transformations suggested by theoretical calculations [37], or both phenomena could occur simultaneously. Raman spectra show drastic changes when approaching the molecular dissociation transition. Just before the transition

to the monatomic phase, a new low-frequency soft mode appears associated with the incommensurate structural and electronic modulation. The behavior of I_2 and Br_2 is very similar; moreover, the vibrational frequencies can be scaled suggesting the generality of the observed successive phase transition mechanism for the molecular dissociation [33].

The example of nitrogen reveals more complexity in high-pressure behavior, because in this case there is an additional possibility for creating the material with covalent bonding—single bonded polymeric phase [38]. The additional complexity is also added by extraordinary rich polymorphic behavior of molecular nitrogen revealed by Raman spectroscopy [39–43]. The triply bonded N_2 molecule is expected to destabilize at pressure above 50 GPa [38, 44], but Raman and infrared absorption (IR) experiments show its tenacious stability up to 170 GPa at 300 K (200 GPa at 80 K) [45, 46]. This behavior is because of kinetic boundaries between different classes of molecular and nonmolecular nitrogen phases [38]. Raman spectroscopy is a powerful technique to study numerous solid-solid phase transitions and metastability phenomena in nitrogen (and other molecular materials, see below) as it is very sensitive to minor changes in the crystal structure. This is because of the sensitivity of the Raman selection rules to the presence of atomic sites with different symmetry, and also to the vibrational coupling and the orientational ordering [40, 47]. Finally, Raman spectroscopy data (along with X-ray diffraction) were revealing in identifying the monatomic polymeric phase—cg-nitrogen. This transformation was found to occur abruptly above 110 GPa based on combined data of different research [28, 41, 48, 49]. This peculiar pressure dependence confirms that molecular dissociation is a volume-driven process that results in destabilization of the molecular orbitals. The associated with the molecular dissociation fluid-fluid transition was reported based on the results of shock-wave experiments [50] and theoretical calculations [51, 52]; this phenomena need to be studied in static high-pressure experiments to provide better insight into their nature as static experiments can allow more informative diagnostic tools. This topic will pose a challenge for the classical Raman spectroscopy tools in the years to come.

Nitrogen is also an excellent example of usefulness of Raman spectroscopy for determination of the melting line. The basis of this is a change in the vibrational selection rules in a fluid state. Indeed, one can expect that the phonon modes (translational intermolecular vibrations) should disappear in the fluid molecular phase because of a lack of translational order of the molecular centers of gravity. However, these observations can be confused with phenomena that accompany the transformation to an orientationally disordered solid phase (plastic phase). Fortunately, in the case of nitrogen there are concomitant with the melting changes in the Raman spectra of molecular vibrons (intramolecular vibration) that allow performing more definitive diagnostics. Indeed, solid molecular nitrogen phases show the presence of two major vibron modes (ν_1 and ν_2) [53] corresponding to different site symmetries which exist in these structures; these result from slightly different intramolecular bond lengths and intermolecular arrangement and, therefore, in

different vibrational frequencies. Naturally, this distinction vanishes in the fluid phase, which results in a single vibron mode (close in frequency to ν_2) and is accompanied by an abrupt small frequency change of ν_2 . A discontinuity in the vibron frequency is a typical phenomenon associated with phase transitions in molecular materials; it usually stems from changes in intermolecular coupling (e.g., [54]). A broadening of the vibron mode can be used as an additional diagnostic of melting [28]. This additional broadening is because the molecules in the fluid phase experience time-dependent thermally-induced bond length variations related to instantaneous changes in the local environment. The ultimate test for the Raman melting diagnostics should be provided by other experimental techniques such as, X-ray diffraction measurements of the diffuse scattering ring [21, 55].

Raman spectroscopy of an ensemble of vibrational modes in the hydrogen isotopes (H_2 and D_2) has been extensively used for the past decades to probe the phase diagram of this system at very high pressures. The experimentally accessed portion of the hydrogen phase diagram (<310 GPa at 100 K [16]) reveals three major solid molecular phases: orientationally disordered phase I and two partially or completely ordered high-pressure low-temperature phases II and III [56] (Figure 2). The presence in the Raman spectra of a series of rotational transitions (rotons) is the manifestation of the fluid or solid phase with freely rotating molecules. The Raman rotational transitions are described by quantum statistics governed by J —the total angular quantum momentum number [57]. The departures from this simple model increase gradually with compression. The transition in phase II (or broken-symmetry phase, BSP) occurs due to an increase in anisotropic intermolecular interaction, which results in a change in the rotational ground state, which is no longer spherical [58]. This quantum ordering transition is exhibited by drastic changes in the Raman spectra of rotons and the vibron-roton coupled modes (vibron sidebands) [59] and appearance of the restricted rotational motion modes (librons) [60]. The low-frequency Raman spectra further change in phase III, where a number of narrow libron/phonon modes supersede the roton mode remnants manifesting the transition to a classically orientationally ordered phase [61]. The behavior of the phonon mode (corresponding to the out-of-phase lateral translational intermolecular vibrations) is less informative for the phase transitions; the steady increase of this mode shows an increase in the intermolecular coupling with compression.

Although these abrupt changes in the rotational Raman spectra with pressure are quite revealing for diagnostics of the molecular rotational and orientational states, their observations are rather experimentally challenging. Thus, Raman (and also IR) spectroscopy of the molecular vibron (which is easier to observe) was used to map out the phase boundaries in the majority of studies (Figure 2). The vibron frequency shows an abrupt discontinuity at the transition to phases II and III, and also between phases II and III [61, 62]. The observations of additional solid phases of hydrogen suggested initially theoretically [64] and experimentally [62] remain illusive [63, 65, 66]. The

FIGURE 2: High-pressure phase diagrams of hydrogen and deuterium. Open circles are Raman, and open squares are IR data for hydrogen. Filled circles are Raman data for deuterium. Lines are guides to the eye. The pressures determined in original publications [61, 62] have been corrected as described in [63].

transition to phase III at 300 K is expected to be observed above 180 GPa, but this regime remains unexplored. The value of the vibron frequency discontinuity varies from a few wavenumbers ($<15\text{ cm}^{-1}$) to over 100 cm^{-1} for the I-II and II-III transitions, respectively (Figure 3). The increased value of the vibron discontinuity for the transition in phase III arises from a modification of inter- and intramolecular interactions related to orientational ordering and structural changes at the transitions [61]. Moreover, phase III is characterized by greatly increased IR activity, which evidences for the orientational ordering with asymmetric atomic site symmetries [67–69].

Vibrational spectroscopy remains the key diagnostics of the state and structure of dense hydrogen to megabar (100 GPa) pressures. The structures of phases II and III still needed to be determined unambiguously since the available X-ray and neutron diffraction data [70, 71] are not sufficient for this purpose. Measurements of vibrational and optical properties of hydrogen have been extended to 315 GPa at 100 K [16], but the study at higher temperatures still remain technically very challenging. Indeed, there is no published report on hydrogen above 200 GPa at room temperature.

The important feature of the vibron behavior at high pressures is a steady decrease of both Raman (Figure 3) and IR active vibrons, which indicate the approach of molecular dissociation, as this phenomenon is related to a partial charge transfer due to an increased coupling of the molecular orbitals through the intermolecular bonds. It is interesting to note that the vibron softening, which was suggested as a “harbinger” of the molecular dissociation [72], is not a

FIGURE 3: (a) Pressure dependence of the Raman vibron in D_2 . (b) The shift of the Raman frequency associated with the II-I transition.

common phenomenon as I_2 and Br_2 do not essentially reveal it [33]. Instead, other modes have been shown to soften near the transition to a monatomic state [33]. Future studies of hydrogen (H_2 and D_2) will show if this low-frequency phonon softening is a common feature of the transition to monatomic state or other more diffusive phase transition mechanisms can be also realized.

Given a great success of Raman spectroscopy for mapping the phase diagram and unraveling the bond properties of hydrogen at high pressures and low temperatures, one might expect that Raman spectroscopy can also be effectively applied for studies of hydrogen at high pressures and temperatures approaching the fluid phase and the plasma transition [73–75]. The hydrogen vibron has been shown to soften substantially at high temperatures [76], and the melting transition has been diagnosed from a small vibron discontinuity [77]. Recent Raman study of hydrogen in the laser heated DAC revealed a large negative vibron frequency discontinuity near the melting line [24] (Figure 4). This has been accompanied by a large broadening and decrease in intensity of the roton bands [24]. These results suggest the existence of a pressure-induced transformation in the fluid, which might be related to the presence of a temperature maximum in the melting line as a function of pressure [73, 77, 78]. Previous Raman studies in the laser-heated DAC [76] also suggested the existence of such fluid with modified intramolecular bonds; moreover, it has been proposed that pairing fluctuations of nuclei may play an important role in such fluid states [79]. Future studies in the high P - T regime probing these states may require an improved diagnostic techniques and perhaps a different experimental strategy (e.g., pump-probe methodology). Indeed, classical Raman spectroscopy can only provide information about the time-averaged material properties, while the information about the dynamical properties appears to be very important in this case.

3.2. Chemical Reactivity of Simple Molecules under Extreme P - T Conditions. Knowledge of the physical and chemical properties of simple molecules such as water and methane under extreme conditions of pressure and temperature is essential to accurately model processes occurring in the interiors of a range of planets including Earth, Uranus, and Neptune [80]. Similar conditions are also generated by shocks and high explosive detonations [81]. It has been suggested that ice VII might also exist in cold subducting slabs in the Earth's mantle [82]. The high magnetic fields of Uranus and Neptune measured by the Voyager 2 spacecraft have been attributed to conductive hot ices [83]. The speciation of carbon in the Earth's interior is critical for understanding the origin of petroleum [84]. Formation and stability of methane under conditions corresponding to the Earth's upper mantle have been demonstrated in recent years [84–86] but the formation of heavier alkanes still remains controversial.

Raman spectroscopy in resistively and laser-heated DAC has been proven to be very informative for study of chemical transformations of simple molecules under extreme P - T conditions. It is especially true for the molecules, which contain hydrogen as another popular technique—X-ray diffraction—is commonly not informative about the crystallographic positions hydrogen takes because of very low X-ray form factor of hydrogen.

The strength of Raman spectroscopy for water is that it is capable to probe the P - T -dependent intra- and intermolecular bonding (e.g., hydrogen bonds); moreover, phase transformations and related to them orientational order-disorder phenomena can be readily recorded [29, 87]. Here we will concentrate on the behavior of water in the high-pressure limit of dissociation and ionization. Ice VII is a dense orientationally disordered cubic phase which is stable in a wide P - T stability field (2–55 GPa). At higher pressures protons first become dynamically disordered along the line

FIGURE 4: Representative temperature-dependent Raman spectra of H_2 obtained in the laser-heated DAC. Left and right panels correspond to the spectral ranges of rotational and vibrational transitions. The curves at each temperature correspond to the same measurement. The vibron amplitude at 300 K is approximately five-times larger than that of the strongest roton band. The spectral positions of the roton bands $S_0(J)$ are shown with vertical ticks. The phonon band is marked by an arrow.

connecting the oxygen atoms (ice VII, [88]), and then take the central positions between oxygens (symmetric ice X, [89]). Raman spectroscopy (along with IR spectroscopy, see [90–93]) was very useful in unraveling this behavior, which was identified through the observations of the softening of the O-H modes associated with the strengthening of the hydrogen bonds, broadening of all vibrational modes and their concentration at low frequencies, and finally the appearance of the characteristic vibrations of the ionic ice X [94].

Raman spectra of hot ice VII show drastic changes upon heating in the region of the O-H stretch [19]. The frequencies of components of the O-H band increase with temperature and the spectral weight moves to higher frequencies (Figure 5) indicating that the hydrogen bond in ice VII weakens as the melting transition is approached and molecules acquire larger translational disorder. To determine the melting of ice VII, the behavior of the translational (phonon) mode has been monitored. This band broadens significantly and changes shape (additional intensity appears at lower frequencies as the result of a breakdown of the wave-vector conservation rule) when melting occurs, while in the solid phase the corresponding degree of temperature-induced broadening is very moderate. Concomitantly, changes also occur in the O-H band: a broad doublet is observed in the fluid that has a different intensity distribution compared to that in ice VII (see also [95]). The phonon mode of ice VII broadens substantially at 53 GPa and 300 K and upon heating

at lower pressures (see also [94]) due to transformation to a dynamically disordered ice VII'; these changes allow tracing the corresponding transformation line.

The phase diagram of water determined by Raman spectroscopy under high P - T conditions show the presence of a triple point between fluid water, ice VII, and ice VII' (see also [96, 97]). Accordingly, the change in the slope of the melting line at this point suggests major differences between thermodynamic properties of ice VII and ice VII'. Therefore, it has been speculated that ice VII' at high temperatures is superionic—the solid state with highly mobile protons and ordered (in a bcc lattice) oxygen ions [98]. Fluid water in this compression regime is expected to be highly ionized given the progressively increased difference in density between solid and fluid state and very weakly pressure-dependent melting curve near the triple point [55]. It has been inferred that water molecules are essentially dynamically dissociated under these conditions as the molecular lifetime becomes comparable to the vibrational period [19]. The Raman spectroscopic data summarized here are firmly supported by the results of the first principle theoretical calculations [19, 99]. However, the differences in melting temperatures determined in different experiments [19, 96, 97] and between theoretical calculations and some experiments [100] call for continuing studies.

Raman spectroscopy is very sensitive to monitor the chemical reactivity even in the case when minuscule amount of materials has experienced the transformation. Raman

FIGURE 5: The temperature dependence of Raman spectra of H_2O at 50 GPa. Pressure was measured at room temperature. The Raman spectra are normalized using a white light source of known spectral distribution. The Raman signal corresponding to the second-order scattering from the diamond anvils is subtracted [94]. The shaded area masks a numerical artifact due to this procedure in the vicinity of the diamond second-order peak. The rectangle centered near 1332 cm^{-1} masks differential peculiarities associated with the subtraction of the diamond first-order peak. Arrows show the tendencies in temperature dependencies of the O-H stretch components.

spectroscopic study of the laser-heated methane under upper-mantle P - T conditions revealed the formation of saturated hydrocarbons containing 2–4 carbons (ethane, propane, and butane) and molecular hydrogen and graphite [101]. Conversely, exposure of ethane to similar conditions results in the production of methane (in addition to heavier hydrocarbons), suggesting that the synthesis of saturated hydrocarbons is reversible. These results support the suggestion that hydrocarbons heavier than methane can be produced by abiogenic processes in the upper mantle [101] (see also [102]). Prior to this work, ethane synthesis has been demonstrated in laser-heated DAC experiments on methane above 1200 K at pressures higher than 10 GPa [103].

The Raman signatures of heavier hydrocarbons are weak but extremely robust as the spectra in the spectral range corresponding to the skeleton C-C vibrations are very individual for hydrocarbons with different carbon compositions, intramolecular bonding, and molecular geometry (cyclic or chain-like). Moreover, this identification is confirmed by observations of the C-H deformation modes, which differ for the saturated hydrocarbons of different length.

3.3. Metals, Magnetic Materials, and High-Temperature Superconductors (HTS). Raman studies of metals are a

challenging task because only a very thin surface layer of the sample (skin depth is smaller than $1000\text{ \AA}$) is typically probed by the exciting laser radiation. The author refers the reader to our previous review papers on the subject [5, 6]. Although the experimental capabilities remained essentially unchanged since the time of publishing of these review papers, the field has progressed substantially as new research has been performed on samples that were well characterized by other techniques. Here the author reviews recent works on metals (Co and Os), high-temperature superconductors ($\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+x}$), and a parent compound for the colossal magnetoresistance materials (LaMnO_3).

Application of Raman spectroscopy to measurements of the shear elastic modulus in hcp metals has been discussed in great details on examples of Fe and Re [6, 10, 11]. Unlike ϵ -Fe (which is nonmagnetic), Co represents an interesting case of ferromagnetic metals, which is expected to transform to a nonmagnetic fcc phase (β -Co) under very high pressures ($>105\text{ GPa}$) [104], but the behavior of the magnetic moments as a function of pressure remained unknown until quite recently because use of the direct experimental technique (X-ray magnetic circular dichroism, XMCD) is challenging under high pressures [105]. Recent XMCP measurements show that Co remains magnetic in the entire pressure domain of stability of ϵ -phase, and the magnetic moments show a steady decrease with pressure [106]. Impulsive stimulated light scattering and Raman spectroscopy measurements revealed a departure from a common linear behavior of the elastic constants as a function of density [107], which indicate a gradual loss of magnetic moments in approaching the transition to β -Co (fcc). This softening of the elastic moduli with pressure has been also confirmed by the results of the inelastic X-ray scattering measurements [108]. The behavior of the vibrational frequency and the elastic constants are essentially different for the isostructural Co and Fe [107] (Figure 6), which makes the use of Co as the analog of Fe for single-crystal studies under high pressures problematic.

High-temperature superconductors (HTS) and materials with large electronic correlations reveal sizable electronic Raman scattering (ERS) cross-sections [109]. This is unlike the situation in metals, which normally show a very weak ERS because the probed momentum space $\mathbf{q} \sim 1/\delta$ (δ is the penetration depth, which is usually of the order of 10–100 nm for visible wavelengths) is very small and because of the screening of the charge fluctuations. Nevertheless, transition metals have been found to exhibit relatively strong ERS due to the presence of anisotropic Fermi-surface (FS). This allows a number of interband transitions to be visible by Raman spectroscopy in the wide frequency range $\omega < v_F/\delta$ (v_F is the electron Fermi velocity) under an assumption of $\omega > \Gamma$ (Γ is the frequency-dependent damping of the electronic state), that is in a clean limit [110]. Thus, Raman spectroscopy can be used as a tool to study the FS topography. For this, ERS should be studied for different $\mathbf{q}$ values and directions. These can be controlled by changing the excitation wavelength and by choosing the scattering geometry. In addition to ERS, the phonon mode behavior

FIGURE 6: Raman frequencies of Co [107] and Fe [10] as a function of pressure.

can be studied. The E_{2g} phonon in Os demonstrated an anomalous $\mathbf{q}$ -dependent softening, broadening, and asymmetry at low temperatures [111]. This finding suggests the occurrence of the Landau damping threshold [112]. The effect occurs in the momentum range corresponding to a crossing of the electron and phonon excitation energies.

The application of pressure may modify both the electronic band structure near the Fermi level and internal scattering processes, which would affect the Raman spectra. An anomalous increase in the electronic light-scattering cross-section was found in Os the pressure range of 20–30 GPa with green and blue excitation wavelengths [113]. At these conditions, an appearance of well-defined electronic peaks at 580 cm^{-1} for the wave-vector direction $\mathbf{q} \parallel [0001]$ and at 350 cm^{-1} for $\mathbf{q} \parallel [10\bar{1}0]$ has been observed. These observations provide evidence for the increase in the damping of the electronic states for large wave vectors $\mathbf{q}$, an essential part of which is probed by the high-energy excitation. Moreover, the anomalies of the optical phonon self-energies were also found in the pressure range of 20–30 GPa. The first-principle band-structure calculations suggest changes in the FS topology that occur due to the E_{2g} phonon displacements (Figure 7). Thus, one can speculate that these phenomena are responsible for the anomalies observed by Raman spectroscopy [113] and in the lattice parameters [114] above 20 GPa.

Raman spectroscopy is very sensitive to the local atomic structure even in the case of a transient local order. This has been exploited in a Raman study of LaMnO_3 —the parent compound for many doped manganites which exhibit colossal magnetoresistance (CMR). High-pressure, low-temperature Raman measurements performed on LaMnO_3 up to 34 GPa provide the first experimental evidence for the persistence of the Jahn-Teller distortion over the entire stability range of the insulating phase [115]. This result

FIGURE 7: Band structure of Os obtained within the LDA approach with spin-orbit coupling at $P = 50 \text{ GPa}$. The red solid and green dashed lines are the band structures calculated for distorted structures obtained by the opposite atomic displacements corresponding to the X-polarized component of the degenerate E_{2g} modes. Fermi level is at zero energy [113].

demonstrates that LaMnO_3 is not a classical Mott insulator as has been suggested earlier [116]. Domains of distorted and undistorted octahedra are present up to 32 GPa, and a weak signal from distorted octahedra is even observed in the metallic state at 34 GPa at 10 K. The insulator-metal transition begins when the number of symmetric octahedral domains increases beyond a critical threshold. The Raman spectra of a peak corresponding to undistorted octahedra show the asymmetry above 32 GPa, which may be associated with a Fano resonance occurring at the onset of the metallic phase, a phenomenon which has been previously observed in several manganite compounds [117, 118].

In HTS, Raman spectroscopy is an excellent tool to probe the electronic properties, including the electron-phonon coupling. Moreover, as a contactless probe separable from its surroundings, Raman spectroscopy circumvents the difficulties that prevent conventional methods from investigating a quantum critical point under pressure. Pressure, being a continuous, reversible, and laboratory-controlled physical variable, can tune properties of a single sample thereby studying the phenomena of interest in details. For example, pressure has been applied to underdoped insulating parent compound of the cuprates $\text{Bi}_{1.98}\text{Sr}_{2.06}\text{Y}_{0.68}\text{Cu}_2\text{O}_8$ [119] to determine the generic phase diagram of HTS by tuning the carrier concentration. Raman measurements of the electronic background and collective modes have been used to extract the information about the electronic scattering, short-range magnetic correlation, and electron-phonon coupling. The results show the presence of a single anomaly in electronic, magnetic, and structural properties near 21 GPa. In conventional theory, magnetism, carrier transport, and superconductivity should all show separate transitions. These results establish the presence in copper oxides HTS of a quantum critical point inside the superconducting dome in close similarity to other unconventional superconductors in strongly correlated materials.

In another high-pressure study, pressure has been applied to an optimally doped HTS $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ with three copper-oxygen (Cu-O) conducting layers in a unit cell. The combined superconducting critical temperature (T_C) (using magnetic susceptibility) and Raman spectroscopic studies (Figure 8) under hydrostatic pressure up to 37 GPa reveal an unpredicted superconductivity enhancement above 24 GPa [120]. This observation suggests the presence of a crossover from the competing order to superconductivity in the inner CuO_2 plane. The latter T_C increase occurs as a result of competition between pairing and phase ordering in different CuO_2 planes (e.g., [121]). The observations have important implications for engineering HTS with much higher T_C 's at ambient conditions.

3.4. Pressure Metrology. Raman pressure gauges have attracted a great interest recently [123–126]. These commonly include diamond (usually ^{13}C) and cubic boron nitride (cBN). These materials are very stable structurally and chemically under extreme P - T conditions. They possess a sizable Raman signal when used as the pressure gauges in the DAC pressure chamber under extreme P - T conditions and this signal can be easily separated spectrally and spatially from that of the stressed Raman anvils. These two factors give the Raman pressure sensors important advantages over more widely used fluorescence gauges [127, 128]. Moreover, Raman measurements of the stressed diamonds have been proposed for pressure measurements (e.g., [123]), thus eliminating the need of having a pressure gauge inside the pressure chamber.

Calibrations of these Raman sensors present a difficult problem under the conditions of very high pressures and extreme temperatures. The common strategy is to perform concomitant measurements on a number of pressure gauges in as close as possible hydrostatic pressure conditions. Moreover, the materials themselves can be used as primary calibrants. An accurate pressure scale can be constructed based on determination of pressure from simultaneous density and sound velocity measurements (e.g., [129]) under static conditions using the so-called redundant scheme. This method requires only a relatively small correction from an adiabatic to an isothermal path at room or moderately elevated temperature, so from that point of view it is expected to be more accurate than shock-wave based calibrations [130]. *In situ* high-temperature concomitant Brillouin spectroscopy and X-ray diffraction measurements can be performed on the crystallographically oriented single-crystal specimen. Raman measurements can be performed concomitantly. These experiments are challenging and time consuming; moreover, they require specialized facilities such as, the Brillouin-X-ray bending magnet beamline at the sector 13 at the Advanced Photon Source (APS) at ANL. Such experiments are currently in progress [131].

For the purpose of this paper the author presents here the review of most relevant Raman works on diamond and cBN. The experiments at room temperatures under quasihydrostatic conditions are currently limited to approximately 150 GPa [132, 133]. The frequency data show a small curvature in ν - P coordinates, and they are essentially

FIGURE 8: Representative Raman spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ at 33.6 GPa through the superconducting transition [120].

linear as a function of density, ρ [133, 134]. Thus, the mode Grüneisen parameter is effectively pressure independent. Even at the highest pressure probed, the samples remain in a low-compression regime ($\delta a/a < 8\%$) making expansions in power series very good approximations to represent both the equation of state (EOS) and Raman shift with pressure. Thus, combined Raman spectroscopy-density measurements constrain the high-pressure scale at room temperature. The effect of cooling below 300 K is negligible on both the EOS and the Raman frequency, so this conclusion holds at low temperatures.

Pressure calibration at high temperature is of special interest, as many of the experiments related to geosciences, planetary sciences and other disciplines require reliable pressure measurements at high temperatures. The synchrotron X-ray diffraction and Raman spectroscopy measurements have been performed in cBN to various pressures depending on temperature using a combination of laser, internal, and external resistive heating in the DAC [122, 132, 135, 136]. These data have been recently used to calibrate the fluorescent pressure sensors up to 120 GPa and 700 K [137]. Laser-heating experiments in cBN to 1750 K at a maximum pressure of 40 GPa, and up to 2300 K at 26 GPa to 40 GPa (Figure 9) show that the phonon frequencies can be well modeled by assuming a pressure-dependent quasiharmonic temperature contribution combined with an almost pressure-independent intrinsic contribution [122].

At very high pressures (>150 GPa) measurement of the Raman shift corresponding to the most stressed part of the anvil [138] is arguably the most viable technique for pressure measurements. Although the results have been shown to be dependent on the experimental geometry (culet dimensions [139], and loading axis direction [140]), other techniques suffer from a necessity to have a specialized equipment at the time of experiment (e.g., a tightly focused X-ray synchrotron beam) and from even larger calibration uncertainties. Thus, the Raman technique remains a very practical alternative.

4. Conclusions and Outlook

Raman spectroscopy has been established as one of the most used and powerful technique for high-pressure research in the DAC. The recent developments have improved the sensitivity, the spatial resolution, and, as the result, made it

FIGURE 9: Raman spectra of cBN at elevated temperatures and pressures acquired with alumina (a), and argon (b), as transmitting media, respectively. Spectra are shifted vertically for clarity. Pressure has been measured at room temperature and was assumed to be temperature independent for the experiment shown in panel (b). Lines for the spectra in panel (b) correspond to phenomenological fits (Voigt profiles) [122].

possible to use it as a rapid diagnostic tool including the use for *in situ* laser heating measurements and as portable systems, such as online systems at X-ray synchrotron beamlines. There are prospects for further improvements of the spatial and temporal resolution of the Raman systems applied for high-pressure research. Moreover, very high-throughput low-frequency ($<10\text{ cm}^{-1}$) Raman systems will soon become routinely available.

These technical improvements have enabled multidisciplinary studies, which include material science, physics and chemistry of planetary interior, search for alternative energy sources and carriers, detonation physics and chemistry, and many others. The improved spatial and temporally resolutions will enable study of the chemical reactivity in heterogeneous samples (including mineral interfaces) and other fast processes. This progress is tightly connected to new capabilities of the surface enhanced Raman spectroscopy [141], which remain to be developed. Moreover, the capabilities of time-resolved and pump-probe techniques remain to be further exploited; the use of coherent anti-Stokes Raman spectroscopy (CARS) with the dynamic high-pressure techniques [142, 143] will broaden high-pressure and geoplanetary science applications.

Future prospective scientific directions will call for new developments of the Raman techniques that permit direct probe of these properties *in situ* statically or dynamically using advanced laser sources and detecting techniques. Those include ultrafast lasers and time-resolved detectors with improved spatial and temporally resolution (e.g., streak-cameras). Of particular interest is to develop new capabilities to probe material properties in extremely small quantity and extreme P - T environments that are beyond current reach but could potentially provide new insights into the materials synthesis under nonequilibrium conditions and into the planetary history and structure.

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References

- [1] P. Gillet, R. J. Hemley, and P. F. McMillan, "Vibrational properties at high pressures and temperatures," in *Ultrahigh-Pressure Mineralogy: Physics and Chemistry of the Earth's Deep Interior*, R. J. Hemley, Ed., vol. 37 of *Reviews of Mineralogy*, pp. 525–590, Mineralogical Society of America, Washington, DC, USA, 1998.
- [2] P. F. McMillan, J. Dubessy, and R. J. Hemley, "Applications in Earth, planetary and environmental sciences," in *Raman Microscopy, Development and Applications*, G. Turrell and J. Corset, Eds., pp. 289–365, Academic Press, New York, NY, USA, 1996.
- [3] P. F. McMillan, "Raman spectroscopy in mineralogy and geochemistry," *Annual Review of Earth and Planetary Sciences*, vol. 17, pp. 255–283, 1989.
- [4] R. J. Hemley and R. F. Porter, "Raman spectroscopy at ultrahigh pressures," *Scripta Metallurgica*, vol. 22, no. 2, pp. 139–144, 1988.
- [5] A. F. Goncharov and V. V. Struzhkin, "Raman spectroscopy of metals, high-temperature superconductors and related materials under high pressure," *Journal of Raman Spectroscopy*, vol. 34, no. 7–8, pp. 532–548, 2003.
- [6] A. F. Goncharov, V. V. Struzhkin, E. Gregoryanz et al., "Raman scattering of metals to very high pressures," in *High-Pressure Phenomena, Proceedings of the International School of Physics, "Enrico Fermi" Course CXLVII*, R. J. Hemley, G. L. Chiarotti, M. Bernasconi, and L. Ulivi, Eds., pp. 297–313, IOS Press, Amsterdam, The Netherlands, 2002.
- [7] A. F. Goncharov, V. V. Struzhkin, R. J. Hemley, H. K. Mao, and Z. Liu, "New Techniques for optical spectroscopy at ultra high pressures," in *Science and Technology of High Pressure: Proceedings of AIRAPT-17*, W. J. N. M. H. Manghnani and M. F. Nicol, Eds., pp. 90–95, Universities Press, Hyderabad, India, 2000.
- [8] K. P. J. Williams, G. D. Pitt, B. J. E. Smith, A. Whitley, D. N. Batchelder, and I. P. Hayward, "Use of a rapid scanning stigmatic Raman imaging spectrograph in the industrial environment," *Journal of Raman Spectroscopy*, vol. 25, no. 1, pp. 131–138, 1994.
- [9] R. J. Hemley, P. M. Bell, and H. K. Mao, "Laser techniques in high-pressure geophysics," *Science*, vol. 237, no. 4815, pp. 605–612, 1987.
- [10] S. Merkel, A. F. Goncharov, H. K. Mao, P. Gillet, and R. J. Hemley, "Raman spectroscopy of iron to 152 gigapascals: implications for earth's inner core," *Science*, vol. 288, no. 5471, pp. 1626–1629, 2000.
- [11] H. Olijnyk, A. P. Jephcoat, and K. Refson, "On optical phonons and elasticity in the hcp transition metals Fe, Ru and Re at high pressure," *Europhysics Letters*, vol. 53, no. 4, pp. 504–510, 2001.
- [12] J. M. Tedesco, H. Owen, D. M. Pallister, and D. M. Morris, "Principles and spectroscopic applications of volume holographic optics," *Analytical Chemistry*, vol. 65, no. 9, pp. A441–A449, 1993.
- [13] G. Turrell, M. Delhay, and P. Dhamelincourt, "Characteristics of Raman microscopy," in *Raman Microscopy: Developments and Applications*, G. Turrell, Ed., pp. 27–49, Academic Press, London, UK, 1996.
- [14] T. Erdogan and V. Mizrahi, "Thin-film filters come of age," *Photonics Spectra*, vol. 37, no. 7, pp. 94–100, 2003.
- [15] C. Moser and F. Havermeier, "Ultra-narrow-band tunable laserline notch filter," *Applied Physics B*, vol. 95, no. 3, pp. 597–601, 2009.
- [16] P. Loubeyre, F. Occelli, and R. LeToullec, "Optical studies of solid hydrogen to 320 GPa and evidence for black hydrogen," *Nature*, vol. 416, no. 6881, pp. 613–617, 2002.
- [17] R. Boehler and K. De Hantsetters, "New anvil designs in diamond-cells," *High Pressure Research*, vol. 24, no. 3, pp. 391–396, 2004.
- [18] J. F. Lin, M. Santoro, V. V. Struzhkin, H. K. Mao, and R. J. Hemley, "In situ high pressure-temperature Raman spectroscopy technique with laser-heated diamond anvil cells," *Review of Scientific Instruments*, vol. 75, no. 10, pp. 3302–3306, 2004.
- [19] A. F. Goncharov, N. Goldman, L. E. Fried et al., "Dynamic ionization of water under extreme conditions," *Physical Review Letters*, vol. 94, no. 12, Article ID 125508, 2005.
- [20] P. Gillet, G. Fiquet, I. Daniel, and B. Reynard, "Raman spectroscopy at mantle pressure and temperature conditions experimental set-up and the example of CaTiO₃ perovskite," *Geophysical Research Letters*, vol. 20, no. 18, pp. 1931–1934, 1993.
- [21] V. B. Prakapenka, A. Kubo, A. Kuznetsov et al., "Advanced flat top laser heating system for high pressure research at GSECARS: application to the melting behavior of germanium," *High Pressure Research*, vol. 28, no. 3, pp. 225–235, 2008.
- [22] A. F. Goncharov, J. A. Montoya, N. Subramanian et al., "Laser heating in diamond anvil cells: developments in pulsed and continuous techniques," *Journal of Synchrotron Radiation*, vol. 16, no. 6, pp. 769–772, 2009.
- [23] N. Subramanian, V. V. Struzhkin, A. F. Goncharov, and R. J. Hemley, "A virtual experiment control and data acquisition system for in situ laser heated diamond anvil cell Raman spectroscopy," *Review of Scientific Instruments*, vol. 81, no. 9, Article ID 093906, 2010.
- [24] N. Subramanian, A. F. Goncharov, V. V. Struzhkin, M. Somayazulu, and R. J. Hemley, "Bonding changes in hot fluid hydrogen at megabar pressures," *Proceedings of the National Academy of Sciences*, vol. 108, no. 15, pp. 6014–6019, 2011.
- [25] P. Richet and B. O. Mysen, "High-temperature dynamics in cristobalite (SiO₂) and carnegieite (NaAlSiO₄): a Raman spectroscopy study," *Geophysical Research Letters*, vol. 26, no. 15, Article ID 1999GL900534, pp. 2283–2286, 1999.
- [26] A. F. Goncharov and J. C. Crowhurst, "Pulsed laser Raman spectroscopy in the laser-heated diamond anvil cell," *Review of Scientific Instruments*, vol. 76, no. 6, Article ID 063905, 2005.
- [27] S. Shim, R. Lamm, S. Rekhi et al., "New micro-Raman spectroscopy systems for high-temperature studies in the diamond anvil cell," *Eos, Transactions*, vol. 86, no. 52, p. MR13B-02, 2005.
- [28] A. F. Goncharov, J. C. Crowhurst, V. V. Struzhkin, and R. J. Hemley, "Triple point on the melting curve and polymorphism of nitrogen at high pressure," *Physical Review Letters*, vol. 101, no. 9, Article ID 095502, 2008.
- [29] R. J. Hemley, "Effects of high pressure on molecules," *Annual Review of Physical Chemistry*, vol. 51, pp. 763–800, 2000.
- [30] M. Somayazulu, A. Madduri, A. F. Goncharov et al., "Novel broken symmetry phase from N₂O at high pressures and high temperatures," *Physical Review Letters*, vol. 87, no. 13, Article ID 135504, 2001.

- [31] C. J. Pickard and R. J. Needs, "Highly compressed ammonia forms an ionic crystal," *Nature Materials*, vol. 7, no. 10, pp. 775–779, 2008.
- [32] N. W. Ashcroft, "Dense Hydrogen: the Reluctant alkali," *Physics World*, vol. 8, pp. 43–47, 1995.
- [33] T. Kume, T. Hiraoka, Y. Ohya, S. Sasaki, and H. Shimizu, "High pressure raman study of bromine and iodine: soft phonon in the incommensurate phase," *Physical Review Letters*, vol. 94, no. 6, Article ID 065506, 2005.
- [34] K. Takemura, K. Sato, H. Fujihisa, and M. Onoda, "Modulated structure of solid iodine during its molecular dissociation under high pressure," *Nature*, vol. 423, no. 6943, pp. 971–974, 2003.
- [35] A. San Miguel, H. Libotte, J. P. Gaspard, M. Gauthier, J. P. Itié, and A. Polian, "Bromine metallization studied by X-ray absorption spectroscopy," *European Physical Journal B*, vol. 17, no. 2, pp. 227–233, 2000.
- [36] R. W. Lynch and H. G. Drickamer, "Effect of pressure on the lattice parameters of iodine, stannic iodide, and p-di-iodobenzene," *The Journal of Chemical Physics*, vol. 45, no. 3, pp. 1020–1026, 1966.
- [37] Q. Zeng, Z. He, X. San et al., "A new phase of solid iodine with different molecular covalent bonds," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 105, no. 13, pp. 4999–5001, 2008.
- [38] C. Mailhot, L. H. Yang, and A. K. McMahan, "Polymeric nitrogen," *Physical Review B*, vol. 46, no. 22, pp. 14419–14435, 1992.
- [39] R. Reichlin, D. Schiferl, S. Martin, C. Vanderborgh, and R. L. Mills, "Optical studies of nitrogen to 130 GPa," *Physical Review Letters*, vol. 55, no. 14, pp. 1464–1467, 1985.
- [40] D. Schiferl, S. Buchsbaum, and R. L. Mills, "Phase transitions in nitrogen observed by Raman spectroscopy from 0.4 to 27.4 GPa at 15 K," *Journal of Physical Chemistry*, vol. 89, no. 11, pp. 2324–2330, 1985.
- [41] E. Gregoryanz, A. F. Goncharov, C. Sanloup, M. Somayazulu, H. K. Mao, and R. J. Hemley, "High P-T transformations of nitrogen to 170 GPa," *Journal of Chemical Physics*, vol. 126, no. 18, Article ID 184505, 2007.
- [42] E. Gregoryanz and A. F. Goncharov, "Comment on 'high-pressure melting curve of nitrogen and the liquid-liquid phase transition'," *Physical Review Letters*, vol. 102, no. 4, Article ID 049601, 2009.
- [43] E. Gregoryanz, A. F. Goncharov, R. J. Hemley, H. K. Mao, M. Somayazulu, and G. Shen, "Raman, infrared, and X-ray evidence for new phases of nitrogen at high pressures and temperatures," *Physical Review B*, vol. 66, no. 22, Article ID 224108, pp. 2241081–2241085, 2002.
- [44] A. K. McMahan and R. Lesar, "Pressure dissociation of solid nitrogen under 1 Mbar," *Physical Review Letters*, vol. 54, no. 17, pp. 1929–1932, 1985.
- [45] A. F. Goncharov, E. Gregoryanz, H. K. Mao, Z. Liu, and R. J. Hemley, "Optical evidence for a nonmolecular phase of nitrogen above 150 GPa," *Physical Review Letters*, vol. 85, no. 6, pp. 1262–1265, 2000.
- [46] M. I. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, "Semiconducting non-molecular nitrogen up to 240 GPa and its low-pressure stability," *Nature*, vol. 411, no. 6834, pp. 170–174, 2001.
- [47] R. Bini, M. Jordan, L. Ulivi, and H. J. Jodl, "Infrared and Raman studies on high pressure phases of solid N₂: an intermediate structural modification between ϵ and δ phases," *Journal of Chemical Physics*, vol. 108, no. 16, pp. 6849–6856, 1998.
- [48] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, "Single-bonded cubic form of nitrogen," *Nature Materials*, vol. 3, no. 8, pp. 558–563, 2004.
- [49] M. J. Lipp, J. P. Klepeis, B. J. Baer et al., "Transformation of molecular nitrogen to nonmolecular phases at megabar pressures by direct laser heating," *Physical Review B*, vol. 76, no. 1, Article ID 014113, 2007.
- [50] H. B. Radousky, W. J. Nellis, M. Ross, D. C. Hamilton, and A. C. Mitchell, "Molecular dissociation and shock-induced cooling in fluid nitrogen at high densities and temperatures," *Physical Review Letters*, vol. 57, no. 19, pp. 2419–2422, 1986.
- [51] D. Donadio, L. Spanu, I. Duchemin, F. Gygi, and G. Galli, "Ab initio investigation of the melting line of nitrogen at high pressure," *Physical Review B*, vol. 82, no. 2, Article ID 020102, 2010.
- [52] B. Boates and S. A. Bonev, "First-order liquid-liquid phase transition in compressed nitrogen," *Physical Review Letters*, vol. 102, no. 1, Article ID 015701, 2009.
- [53] R. Lesar, S. A. Ekberg, L. H. Jones, R. L. Mills, L. A. Schwalbe, and D. Schiferl, "Raman spectroscopy of solid nitrogen up to 374 kbar," *Solid State Communications*, vol. 32, no. 2, pp. 131–134, 1979.
- [54] L. Cui, N. H. Chen, and I. F. Silvera, "Excitations, order parameters, and phase diagram of solid deuterium at megabar pressures," *Physical Review B*, vol. 51, no. 21, pp. 14987–14997, 1995.
- [55] A. F. Goncharov, C. Sanloup, N. Goldman et al., "Dissociative melting of ice VII at high pressure," *Journal of Chemical Physics*, vol. 130, no. 12, Article ID 124514, 2009.
- [56] H. K. Mao and R. J. Hemley, "Ultrahigh-pressure transitions in solid hydrogen," *Reviews of Modern Physics*, vol. 66, no. 2, pp. 671–692, 1994.
- [57] I. F. Silvera, "The solid molecular hydrogens in the condensed phase: fundamentals and static properties," *Reviews of Modern Physics*, vol. 52, no. 2, pp. 393–452, 1980.
- [58] I. F. Silvera and R. J. Wijngaarden, "New low-temperature phase of molecular deuterium at ultrahigh pressure," *Physical Review Letters*, vol. 47, no. 1, pp. 39–42, 1981.
- [59] A. F. Goncharov, J. H. Eggert, I. I. Mazin, R. J. Hemley, and H. K. Mao, "Raman excitations and orientational ordering in deuterium at high pressure," *Physical Review B*, vol. 54, no. 22, pp. R15590–R15593, 1996.
- [60] A. F. Goncharov, R. J. Hemley, H. K. Mao, and J. Shu, "New high-pressure excitations in parahydrogen," *Physical Review Letters*, vol. 80, no. 1, pp. 101–104, 1998.
- [61] I. I. Mazin, R. J. Hemley, A. F. Goncharov, M. Hanfland, and H. K. Mao, "Quantum and classical orientational ordering in solid hydrogen," *Physical Review Letters*, vol. 78, no. 6, pp. 1066–1069, 1997.
- [62] A. F. Goncharov, I. I. Mazin, J. H. Eggert, R. J. Hemley, and H. K. Mao, "Invariant points and phase transitions in deuterium at megabar pressures," *Physical Review Letters*, vol. 75, no. 13, pp. 2514–2517, 1995.
- [63] A. F. Goncharov, R. J. Hemley, and H. K. Mao, "Vibron frequencies of solid H₂ and D₂ to 200 GPa and implications for the P-T phase diagram," *Journal of Chemical Physics*, vol. 134, no. 17, Article ID 174501, 4 pages, 2011.
- [64] M. P. Surh, K. J. Runge, T. W. Barbee, E. L. Pollock, and C. Mailhot, "Ab initio calculations for solid molecular hydrogen," *Physical Review B*, vol. 55, no. 17, pp. 11330–11341, 1997.
- [65] B. J. Baer, W. J. Evans, and C. S. Yoo, "Coherent anti-stokes Raman spectroscopy of highly compressed solid deuterium at 300 K: evidence for a new phase and implications for the

- band gap," *Physical Review Letters*, vol. 98, no. 23, Article ID 235503, 4 pages, 2007.
- [66] B. J. Baer, W. J. Evans, and C. S. Yoo, "Erratum: coherent anti-stokes Raman spectroscopy of highly compressed solid deuterium at 300 K: evidence for a new phase and implications for the Band Gap [Phys. Rev. Lett. 98, 235503 (2007)]," *Physical Review Letters*, vol. 102, no. 20, Article ID 209901, 1 pages, 2009.
- [67] B. Edwards and N. W. Ashcroft, "Spontaneous polarization in dense hydrogen," *Nature*, vol. 388, no. 6643, pp. 652–655, 1997.
- [68] J. S. Tse and D. D. Klug, "Evidence from molecular dynamics simulations for non-metallic behaviour of solid hydrogen above 160 GPa," *Nature*, vol. 378, no. 6557, pp. 595–597, 1995.
- [69] C. J. Pickard and R. J. Needs, "Structure of phase III of solid hydrogen," *Nature Physics*, vol. 3, no. 7, pp. 473–476, 2007.
- [70] I. Goncharenko and P. Loubeyre, "Neutron and X-ray diffraction study of the broken symmetry phase transition in solid deuterium," *Nature*, vol. 435, no. 7046, pp. 1206–1209, 2005.
- [71] Y. Akahama, M. Nishimura, H. Kawamura, N. Hirao, Y. Ohishi, and K. Takemura, "Evidence from X-ray diffraction of orientational ordering in phase III of solid hydrogen at pressures up to 183 GPa," *Physical Review B*, vol. 82, no. 6, Article ID 060101, 2010.
- [72] N. W. Ashcroft, "Pairing instabilities in dense hydrogen," *Physical Review B*, vol. 41, no. 16, pp. 10963–10971, 1990.
- [73] S. A. Bonev, E. Schwegler, T. Ogitsu, and G. Galli, "A quantum fluid of metallic hydrogen suggested by first-principles calculations," *Nature*, vol. 431, no. 7009, pp. 669–672, 2004.
- [74] S. Scandolo, "Liquid-liquid phase transition in compressed hydrogen from first-principles simulations," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 100, no. 6, pp. 3051–3053, 2003.
- [75] M. A. Morales, C. Pierleoni, E. Schwegler, and D. M. Ceperley, "Evidence for a first-order liquid-liquid transition in high-pressure hydrogen from ab initio simulations," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 107, no. 29, pp. 12799–12803, 2010.
- [76] A. F. Goncharov and J. C. Crowhurst, "Raman spectroscopy of hot compressed hydrogen and nitrogen: implications for the intramolecular potential," *Physical Review Letters*, vol. 96, no. 5, 2006.
- [77] E. Gregoryanz, A. F. Goncharov, K. Matsuishi, H. K. Mao, and R. J. Hemley, "Raman spectroscopy of hot dense hydrogen," *Physical Review Letters*, vol. 90, no. 17, pp. 175701/1–175701/4, 2003.
- [78] F. Datchi, P. Loubeyre, and R. LeToullec, "Extended and accurate determination of the melting curves of aragon, helium, ice (H₂O), and hydrogen (H₂)," *Physical Review B*, vol. 61, no. 10, pp. 6535–6546, 2000.
- [79] A. F. Goncharov and J. Crowhurst, "Proton delocalization under extreme conditions of high pressure and temperature," *Phase Transitions*, vol. 80, no. 10–12, pp. 1051–1072, 2007.
- [80] W. B. Hubbard, W. J. Nellis, A. C. Mitchell, N. C. Holmes, S. S. Limaye, and P. C. Mccandless, "Interior structure of Neptune: comparison with Uranus," *Science*, vol. 253, no. 5020, pp. 648–651, 1991.
- [81] L. E. Fried, M. R. Manaa, P. F. Pagoria, and R. L. Simpson, "Design and synthesis of energetic materials," *Annual Review of Materials Science*, vol. 31, pp. 291–321, 2001.
- [82] C. R. Bina and A. Navrotsky, "Possible presence of high-pressure ice in cold subducting slabs," *Nature*, vol. 408, no. 6814, pp. 844–847, 2000.
- [83] N. F. Ness, M. H. Acuna, K. W. Behannon et al., "Magnetic fields at Uranus," *Science*, vol. 233, no. 4759, pp. 85–89, 1986.
- [84] H. P. Scott, R. J. Hemley, H. K. Mao et al., "Generation of methane in the Earth's mantle: in situ high pressure-temperature measurements of carbonate reduction," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 101, no. 39, pp. 14023–14026, 2004.
- [85] J. F. Kenney, V. A. Kutcherov, N. A. Bendeliani, and V. A. Alekseev, "The evolution of multicomponent systems at high pressures: VI. The thermodynamic stability of the hydrogen-carbon system: the genesis of hydrocarbons and the origin of petroleum," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 99, no. 17, pp. 10976–10981, 2002.
- [86] J. Y. Chen, L. J. Jin, J. P. Dong, H. F. Zheng, and G. Y. Liu, "Methane formation from CaCO₃ reduction catalyzed by high pressure," *Chinese Chemical Letters*, vol. 19, no. 4, pp. 475–478, 2008.
- [87] J. D. Frantz, J. Dubessy, and B. Mysen, "An optical cell for Raman spectroscopic studies of supercritical fluids and its application to the study of water to 500°C and 2000 bar," *Chemical Geology*, vol. 106, no. 1–2, pp. 9–26, 1993.
- [88] M. Benoit, A. H. Romero, and D. Marx, "Reassigning hydrogen-bond centering in dense ice," *Physical Review Letters*, vol. 89, no. 14, Article ID 145501, 2002.
- [89] W. B. Holzapfel, "On the symmetry of the hydrogen bonds in ice VI," *Journal of Chemical Physics*, vol. 56, no. 2, pp. 712–715, 1972.
- [90] A. F. Goncharov, V. V. Struzhkin, M. S. Somayazulu, R. J. Hemley, and H. K. Mao, "Compression of ice to 210 gigapascals: infrared evidence for a symmetric hydrogen-bonded phase," *Science*, vol. 273, no. 5272, pp. 218–220, 1996.
- [91] M. Song, H. Yamawaki, H. Fujihisa, M. Sakashita, and K. Aoki, "Infrared absorption study of Fermi resonance and hydrogen-bond symmetrization of ice up to 141 GPa," *Physical Review B*, vol. 60, no. 18, pp. 12644–12650, 1999.
- [92] V. V. Struzhkin, A. F. Goncharov, R. J. Hemley, and H. K. Mao, "Cascading fermi resonances and the soft mode in dense ice," *Physical Review Letters*, vol. 78, no. 23, pp. 4446–4449, 1997.
- [93] K. Aoki, H. Yamawaki, M. Sakashita, and H. Fujihisa, "Infrared absorption study of the hydrogen-bond symmetrization in ice to 110 GPa," *Physical Review B*, vol. 54, no. 22, pp. 15673–15677, 1996.
- [94] A. F. Goncharov, V. V. Struzhkin, H. K. Mao, and R. J. Hemley, "Raman spectroscopy of dense H₂O and the transition to symmetric hydrogen bonds," *Physical Review Letters*, vol. 83, no. 10, pp. 1998–2001, 1999.
- [95] J. F. Lin, B. Militzer, V. V. Struzhkin, E. Gregoryanz, R. J. Hemley, and H. K. Mao, "High pressure-temperature Raman measurements of H₂O melting to 22 GPa and 900 K," *Journal of Chemical Physics*, vol. 121, no. 17, pp. 8423–8427, 2004.
- [96] J. F. Lin, E. Gregoryanz, V. V. Struzhkin, M. Somayazulu, H. K. Mao, and R. J. Hemley, "Melting behavior of H₂O at high pressures and temperatures," *Geophysical Research Letters*, vol. 32, no. 11, Article ID L11306, pp. 1–4, 2005.
- [97] B. Schwager, L. Chudinovskikh, A. Gavriluk, and R. Boehler, "Melting curve of H₂O to 90 GPa measured in a laser-heated diamond cell," *Journal of Physics Condensed Matter*, vol. 16, no. 14, pp. S1177–S1179, 2004.

- [98] C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, and M. Parrinello, "Superionic and metallic states of water and ammonia at giant planet conditions," *Science*, vol. 283, no. 5398, pp. 44–46, 1999.
- [99] N. Goldman, L. E. Fried, I. F. W. Kuo, and C. J. Mundy, "Bonding in the superionic phase of water," *Physical Review Letters*, vol. 94, no. 21, Article ID 217801, pp. 1–4, 2005.
- [100] E. Schwegler, M. Sharma, F. Gygi, and G. Galli, "Melting of ice under pressure," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 105, no. 39, pp. 14779–14783, 2008.
- [101] A. F. Goncharov, A. Kolesnikov, and V. G. Kutcherov, "Methane-derived hydrocarbons produced under upper-mantle conditions," *Nature Geoscience*, vol. 2, no. 8, pp. 566–570, 2009.
- [102] D. H. Eggler and D. R. Baker, "Reduced volatiles in the system C-O-H: implications in mantle melting, fluid formation, and diamond genesis," in *High-Pressure Research in Geophysics*, S. Akimoto and M. H. Manghnani, Eds., vol. 12 of *Advances in Earth and Planetary Sciences*, pp. 237–250, Center for Academic Publications, Tokyo, Japan, 1982.
- [103] H. Hirai, K. Konagai, T. Kawamura, Y. Yamamoto, and T. Yagi, "Polymerization and diamond formation from melting methane and their implications in ice layer of giant planets," *Physics of the Earth and Planetary Interiors*, vol. 174, no. 1–4, pp. 242–246, 2009.
- [104] C. S. Yoo, H. Cynn, P. Soderlind, and V. Iota, "New β (fcc)-Cobalt to 210 GPa," *Physical Review Letters*, vol. 84, no. 18, pp. 4132–4135, 2000.
- [105] V. Iota, J. H. P. Klepeis, C. S. Yoo, J. Lang, D. Haskel, and G. Srajer, "Electronic structure and magnetism in compressed 3d transition metals," *Applied Physics Letters*, vol. 90, no. 4, Article ID 042505, 2007.
- [106] N. Ishimatsu, N. Kawamura, H. Maruyama et al., "Paramagnetism with anomalously large magnetic susceptibility in β (fcc)-cobalt probed by X-ray magnetic circular dichroism up to 170 GPa," *Physical Review B*, vol. 83, no. 18, Article ID 180409, 4 pages, 2011.
- [107] A. F. Goncharov, J. Crowhurst, and J. M. Zaug, "Elastic and vibrational properties of cobalt to 120 GPa," *Physical Review Letters*, vol. 92, no. 11, p. 115502, 2004.
- [108] D. Antonangeli, M. Krisch, G. Fiquet et al., "Aggregate and single-crystalline elasticity of hcp cobalt at high pressure," *Physical Review B*, vol. 72, no. 13, pp. 1–7, 2005.
- [109] T. P. Devereaux and R. Hackl, "Inelastic light scattering from correlated electrons," *Reviews of Modern Physics*, vol. 79, no. 1, pp. 175–233, 2007.
- [110] L. A. Falkovsky and S. Klama, "Inelastic light scattering by electrons and plasmons in metals," *Journal of Experimental and Theoretical Physics*, vol. 85, no. 2, pp. 370–375, 1997.
- [111] Y. S. Ponomov, G. A. Bolotin, C. Thomsen, and M. Cardona, "Raman scattering in Os: nonadiabatic renormalization of the optical phonon self-energies," *Physica Status Solidi B*, vol. 208, no. 1, pp. 257–269, 1998.
- [112] I. P. Ipatova and A. V. Subashiev, "Long-wave optical-phonon spectrum in metals and heavily doped semiconductors," *Soviet Physics ZhETF*, vol. 39, pp. 349–355, 1974.
- [113] Y. S. Ponomov, V. V. Struzhkin, A. F. Goncharov, and S. V. Streltsov, "Q-dependent electronic excitations in osmium: pressure- and temperature-induced effects," *Physical Review B*, vol. 78, no. 24, Article ID 245106, 9 pages, 2010.
- [114] F. Occelli, D. L. Farber, J. Badro et al., "Experimental evidence for a high-pressure isostructural phase transition in osmium," *Physical Review Letters*, vol. 93, no. 9, Article ID 095502, 4 pages, 2004.
- [115] M. Baldini, V. V. Struzhkin, A. F. Goncharov, P. Postorino, and W. L. Mao, "Persistence of Jahn-Teller distortion up to the insulator to metal transition in LaMnO_3 ," *Physical Review Letters*, vol. 106, no. 6, Article ID 066402, 4 pages, 2011.
- [116] I. Loa, P. Adler, A. Grzechnik et al., "Pressure-induced quenching of the Jahn-Teller distortion and insulator-to-metal transition in LaMnO_3 ," *Physical Review Letters*, vol. 87, no. 12, Article ID 125501, 2001.
- [117] D. Marrocchelli, P. Postorino, D. Di Castro et al., "Pressure and temperature dependence of the Fano resonance in the Raman spectrum of A_2FeMoO_6 systems ($\text{A}=\text{Sr}, \text{Ca}$)," *Physical Review B*, vol. 76, no. 17, Article ID 172405, 2007.
- [118] J. L. Her, H. L. Liu, C. H. Shen, R. S. Liu, and H. S. Sheu, "Effect of Ca doping on the optical properties of $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$," *Journal of Applied Physics*, vol. 99, no. 1, Article ID 013905, 6 pages, 2006.
- [119] T. Cuk, V. V. Struzhkin, T. P. Devereaux et al., "Uncovering a pressure-tuned electronic transition in $\text{Bi}_{1.98}\text{Sr}_{2.06}\text{Y}_{0.68}\text{Cu}_2\text{O}_{8+\delta}$ using Raman scattering and X-ray diffraction," *Physical Review Letters*, vol. 100, no. 21, Article ID 217003, 2008.
- [120] X. J. Chen, V. V. Struzhkin, Y. Yu et al., "Enhancement of superconductivity by pressure-driven competition in electronic order," *Nature*, vol. 466, no. 7309, pp. 950–953, 2010.
- [121] E. E. M. Chia, J. X. Zhu, D. Talbayev et al., "Observation of competing order in a high- T_c superconductor using femtosecond optical pulses," *Physical Review Letters*, vol. 99, no. 14, Article ID 147008, 2007.
- [122] A. F. Goncharov, J. C. Crowhurst, J. K. Dewhurst, and S. Sharma, "Raman spectroscopy of cubic boron nitride under extreme conditions of high pressure and temperature," *Physical Review B*, vol. 72, no. 10, Article ID 100104, 2005.
- [123] Y. Akahama and H. Kawamura, "Diamond anvil Raman gauge in multimegabar pressure range," *High Pressure Research*, vol. 27, no. 4, pp. 473–482, 2007.
- [124] K. P. Esler, R. E. Cohen, B. Militzer, J. Kim, R. J. Needs, and M. D. Towler, "Fundamental high-pressure calibration from all-electron quantum Monte Carlo calculations," *Physical Review Letters*, vol. 104, no. 18, Article ID 185702, 2010.
- [125] B. O. Mysen, "Speciation and mixing behavior of silica-saturated aqueous fluid at high temperature and pressure," *American Mineralogist*, vol. 95, no. 11–12, pp. 1807–1816, 2010.
- [126] N. Dubrovinskaia, L. Dubrovinsky, R. Caracas, and M. Hanfland, "Diamond as a high pressure gauge up to 2.7 Mbar," *Applied Physics Letters*, vol. 97, no. 25, Article ID 251903, 2010.
- [127] H. K. Mao, J. Xu, and P. M. Bell, "Calibration of the ruby pressure gauge to 800 kbar under quasi hydrostatic conditions," *Journal of Geophysical Research*, vol. 91, no. B5, pp. 4673–4676, 1986.
- [128] F. Datchi, R. LeToullec, and P. Loubeyre, "Improved calibration of the SrB_4O_7 : Sm^{2+} optical pressure gauge: advantages at very high pressures and high temperatures," *Journal of Applied Physics*, vol. 81, no. 8, pp. 3333–3339, 1997.
- [129] C. S. Zha, H. K. Mao, and R. J. Hemley, "Elasticity of MgO and a primary pressure scale to 55 GPa," *Proceedings of the National Academy of Sciences*, vol. 97, no. 25, pp. 13494–13499, 2000.
- [130] W. B. Holzapfel, "Corrigendum," *High Pressure Research*, vol. 25, no. 3, p. 227, 2005.

- [131] A. F. Goncharov, S. Sinogeikin, J. C. Crowhurst et al., "Cubic boron nitride as a primary calibrant for a high temperature pressure scale," *High Pressure Research*, vol. 27, no. 4, pp. 409–417, 2007.
- [132] F. Datchi, A. Dewaele, Y. Le Godec, and P. Loubeyre, "Equation of state of cubic boron nitride at high pressures and temperatures," *Physical Review B*, vol. 75, no. 21, Article ID 214104, 2007.
- [133] F. Occelli, P. Loubeyre, and R. Letoullec, "Properties of diamond under hydrostatic pressures up to 140 GPa," *Nature Materials*, vol. 2, no. 3, pp. 151–154, 2003.
- [134] I. V. Aleksandrov, A. F. Goncharov, I. N. Makarenko, A. N. Zisman, E. V. Yakovenko, and S. M. Stishov, "Diamond and cubic boron nitride under high pressure: Raman scattering, equation of state and high pressure scale," *High Pressure Research*, vol. 1, no. 5-6, pp. 333–336, 1989.
- [135] A. F. Goncharov, J. C. Crowhurst, J. K. Dewhurst et al., "Thermal equation of state of cubic boron nitride: implications for a high-temperature pressure scale," *Physical Review B*, vol. 75, no. 22, Article ID 224114, 2007.
- [136] F. Datchi and B. Canny, "Raman spectrum of cubic boron nitride at high pressure and temperature," *Physical Review B*, vol. 69, no. 14, Article ID 144106, pp. 144106–7, 2004.
- [137] Q. Wei, N. Dubrovinskaia, and L. Dubrovinsky, "Ruby and Sm: YAG fluorescence pressure gauges up to 120 GPa and 700 K," *Journal of Applied Physics*, vol. 110, no. 4, Article ID 043513, 4 pages, 2011.
- [138] M. Hanfland and K. Syassen, "A Raman study of diamond anvils under stress," *Journal of Applied Physics*, vol. 57, no. 8, pp. 2752–2756, 1985.
- [139] B. J. Baer, M. E. Chang, and W. J. Evans, "Raman shift of stressed diamond anvils: pressure calibration and culet geometry dependence," *Journal of Applied Physics*, vol. 104, no. 3, Article ID 034504, 2008.
- [140] Y. Akahama and H. Kawamura, "Raman study on the stress state of [111] diamond anvils at multimegabar pressure," *Journal of Applied Physics*, vol. 98, no. 8, Article ID 083523, 4 pages, 2005.
- [141] K. E. Brown and D. D. Dlott, "High-pressure raman spectroscopy of molecular monolayers adsorbed on a metal surface," *Journal of Physical Chemistry C*, vol. 113, no. 14, pp. 5751–5757, 2009.
- [142] G. Tas, J. Franken, S. A. Hambir, D. E. Hare, and D. D. Dlott, "Ultrafast raman spectroscopy of shock fronts in molecular solids," *Physical Review Letters*, vol. 78, no. 24, pp. 4585–4588, 1997.
- [143] D. S. Moore and S. C. Schmidt, "Vibrational spectroscopy of materials under extreme pressure and temperature," *Journal of Molecular Structure*, vol. 347, pp. 101–111, 1995.
- [144] R. J. Hemley, H. K. Mao, and M. Hanfland, "Spectroscopic investigations of the insulator-metal transition in solid hydrogen," in *Molecular Systems Under High Pressure*, R. Pucci and G. Piccitto, Eds., pp. 223–243, Elsevier Science, North Holland, Amsterdam, 1991.