New phenomena in low-*Z* materials at megabar pressures

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Abstract. We present an overview of selected recent static compression studies of low-Z materials to megabar pressures (>100 GPa). Dense hydrogen shows unexpected complexity as is evident from new spectroscopic transitions and unusual behaviour of the pressure dependence of the ortho–para-hydrogen conversion rate. H_2O-ice exhibits tunnelling effects in a quantum-crystal state before transforming to a statically symmetric hydrogen-bonded structure well above 100 GPa. Studies of dense simple molecular compounds reveal new chemical phenomena and pressure-induced changes in intermolecular interactions. Magnetic susceptibility experiments on sulphur to 160 GPa reveal this material to be the highest-temperature elemental superconductor measured to date.

1. Introduction

Accelerating developments in static high-pressure techniques have brought about major advances in the pressure range over which materials can be studied in the laboratory [1]. These experiments now provide evidence for new physical phases under extreme pressure in many classes of materials, particularly those containing low-atomic-number (Z) elements. Low-Z materials have attracted attention for high-pressure investigations because many are highly compressible, thereby producing a large variation in interatomic or intermolecular distances, because their putatively simple electronic structure provides important tests of theory, and because the lowest-Z components (e.g., hydrogen) can exhibit quantum behaviour manifested in different ways in different regimes of compression [2].

Here we provide a brief overview of some recent developments from our laboratory in studies of this broad class of materials to pressures of 300 GPa and temperatures of 4–300 K. We discuss recent findings about hydrogen, a system with continuing, unexpected complexity at very high pressure, observations of quantum effects in the transformation to the symmetric hydrogen-bonded state of H_2O, new chemical phenomena in simple molecular compounds at high pressure, and pressure-induced superconductivity in chalcogenides. The range of pressure and temperature place the observed material behaviour within the domain of condensed-matter science; nevertheless, striking changes in physical and chemical properties occur that are not yet fully understood theoretically.

2. New excitations in hydrogen

Significant recent progress has been made in the study of dense hydrogen. Stabilization of single crystals at megabar pressures has allowed accurate identification of the crystal structure and measurement of the equation of state to 120 GPa and 300 K [3]. Infrared

and Raman spectroscopy to 300 GPa has revealed that three phases (I, II, and III) are stable at different conditions of pressure and temperature, revealing a rich and intriguing phase diagram [4], and there is a remarkable infrared response of the vibron (intramolecular mode) above 150 GPa [5–8] providing evidence for charge transfer [6] and possibly a novel antiferroelectric transition [9, 10]. We briefly describe several new developments. During the past year, we have extended these vibrational spectroscopic measurements to obtain additional information on the structure and dynamics of the $J = 0$ solids and to gain a clearer understanding of the properties of $J = 1$ and $J = 0$ mixtures, including the ortho–para-hydrogen conversion rate.
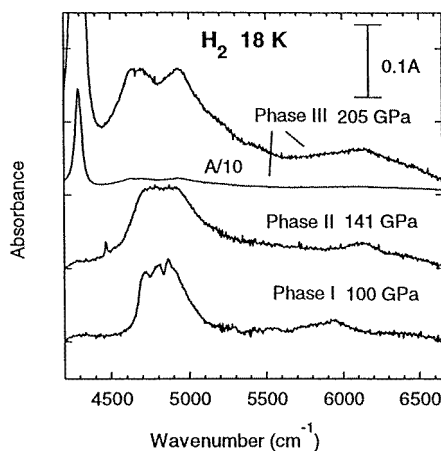

Figure 1. Infrared absorption spectra in the vicinity of the vibron for phases I, II, and III of molecular hydrogen [12].

Natural diamonds were used as anvils in all of the previous spectroscopic studies of hydrogen mentioned above; these diamonds invariably contain impurities that give rise to a background luminescence that prevents measurements of weak signals. In recent work, significant progress was made by eliminating the background signal with ultrapure, synthetic single-crystal diamond anvils. Use of these diamonds has allowed us to observe new classes of vibrational excitations [11]. An example is shown for the pressure dependence of the infrared spectrum in the vicinity of the vibron for para-hydrogen in phases I, II, and III (figure 1). X-ray diffraction indicates that the crystal structure of phase I is hcp [3]. As a result, there is no symmetry-allowed (dipole) transition for the vibron, which should appear near 4500 cm^{-1}. Instead, there are diffuse features assigned to multiphonon bands (e.g., vibrons and rotons). In contrast to the absence of symmetry-allowed vibrons in phase I, a weak infrared vibron is observed in phase II (possibly disorder or strain-induced [11]); this contrasts with the very strong vibron in phase III, as documented previously (e.g., in [5]).

In addition to the infrared measurements, a wealth of new information has been obtained from Raman scattering, particularly in the lower-frequency range [11]. Distinct spectra are observed for each of the three phases (figure 2). The low-frequency excitations are plotted as a function of pressure in figure 3, along with the results of earlier studies [7, 13, 14]. Numerous new features are observed at lower frequencies. A weak pressure shift and crystal-field splitting of the roton modes are observed for phase I. New low-frequency modes are observed for phase II (the broken-symmetry phase); although there is very little pressure shift of the frequencies, changes in relative intensities occur [11]. Very different
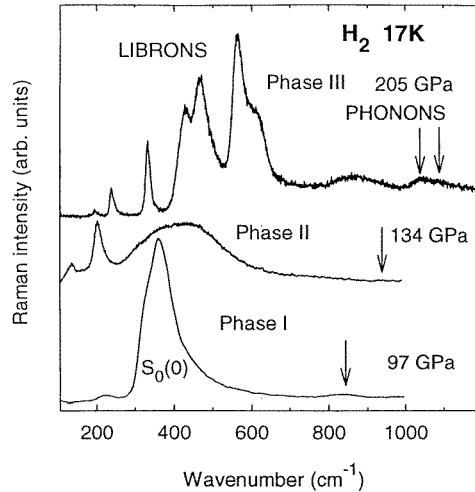
Figure 2. Low-frequency Raman spectra of phases I, II, and III of molecular hydrogen [11].
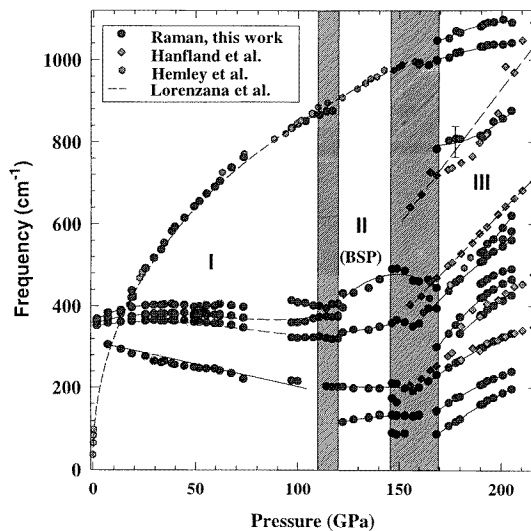

Figure 3. The pressure dependence of low-frequency Raman vibrational modes of para-hydrogen in phases I, II, and III [11, 12] and results from earlier studies of pure para-hydrogen [14] and samples starting out as ortho–para-hydrogen mixtures at 80 K [7, 13]. BSP denotes the broken-symmetry phase (phase II).

pressure shifts in phase III are observed. The earlier data for samples starting out as ortho–para-hydrogen mixtures are close to the measurements obtained for the pure para-hydrogen samples, and confirm that bands observed to higher frequencies relative to the vibron in the infrared spectrum (figure 1) are vibron–libron combination bands. The data give evidence for quantum mechanical behaviour for phases I and II. In contrast, the system appears to exhibit classical-like behaviour in phase III as a result of the stronger intermolecular interactions in this phase [4, 11].

3. The pressure dependence of the ortho–para-hydrogen conversion

Another important and surprising result that emerged from recent studies of dense hydrogen is the unusual behaviour of the ortho–para-hydrogen conversion rate with pressure. Because of the coupling between rotational states and nuclear spins, one can measure the conversion from the rotational Raman spectrum [15]. Ortho–para-hydrogen conversion requires a magnetic field gradient acting on a molecule to flip a proton spin [16]. This is supplied by ortho-hydrogen molecules ($I = 1$), and the rate of conversion is proportional to the average number of ortho-hydrogen neighbours. However, this is only valid if there is rapid molecular diffusion and the distribution of ortho-hydrogen molecules continues to be random. A Monte Carlo model was used to account for the conversion in the absence of molecular diffusion and found to fit the temporal evolution of the spectra from minutes to long times (e.g., tens of hours).
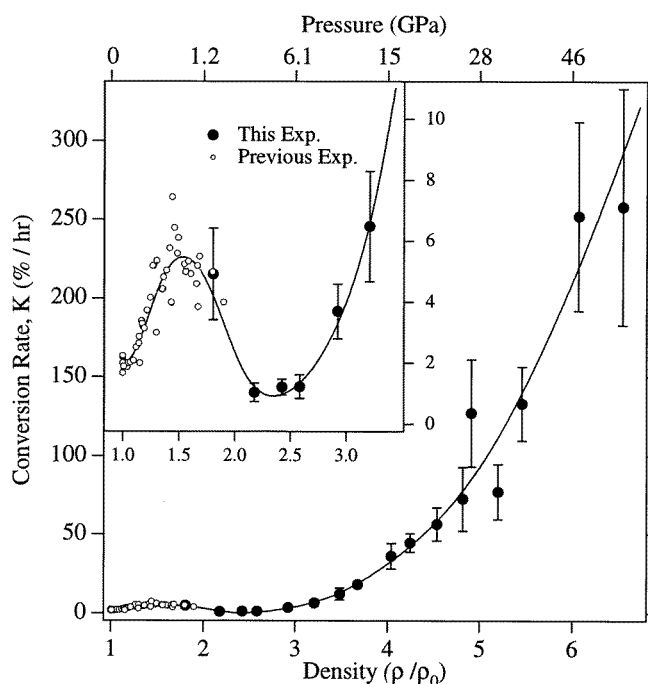

Figure 4. The pressure dependence of the ortho–para-hydrogen conversion rate. The new data show the results from Eggert *et al* [15]. The open circles are from previous low-pressure studies (see reference [15]), and the solid line is a guide to the eye [17].

The conversion rate obtained from the analysis shows an unusual non-monotonic behaviour as a function of pressure (figure 4) [15]. Consistently with previous work, our finding is that the conversion rate increases to a maximum at about 1 GPa and then decreases. The new results show that there is a minimum at about 3 GPa followed by a dramatic increase that continues to at least 58 GPa. An energy $E = 2B = 171$ K needs to be absorbed by the lattice on conversion of a molecule in the ground state from ortho-hydrogen to para-hydrogen. Berlinsky [17] showed that one-phonon conversion should increase with pressure, then fall as a result of the decrease in density of states. Thus, the rapid increase observed above 3 GPa requires a new channel. We suggest that pressure-

induced broadening of the $J = 2$ roton band is a likely mechanism, but this remains to be established quantitatively.

4. H_2O-ice

H_2O is a ubiquitous low-Z material, and one that is exhibits remarkable high-pressure properties, including pressure-induced molecular dissociation and concomitant quantum behaviour. Synchrotron x-ray diffraction and infrared spectroscopy to 210 GPa have established that H_2O-ice transforms to a non-molecular state at these very high pressures [18, 19]. The x-ray measurements, which are principally sensitive to the oxygen positions, have shown that the oxygen sublattice can be interpreted as close to body-centred cubic, consistent with earlier measurements to 128 GPa [20]. Figure 5 shows the pressure–volume relations at room temperature obtained from x-ray diffraction, including both new and earlier data, along with lower-pressure curves for liquid water, ice VI, ice VII, and the high-pressure form, called ice X. Notably, the material has very high initial compressibility before reaching the highest-pressure form.

Infrared reflectance spectra show that in the highest-pressure form, the conventional covalent OH and hydrogen bonds that characterize ice, and water are radically altered [18]. Figure 6(a) shows the imaginary part of the dielectric function, ϵ_2, obtained by transforming the infrared reflectivity spectra. The simple spectrum at the highest pressure is consistent with both the spectroscopic and diffraction data, with the theoretically predicted non-molecular form having the Cu_2O-structure symmetrized hydrogen bonds. The results
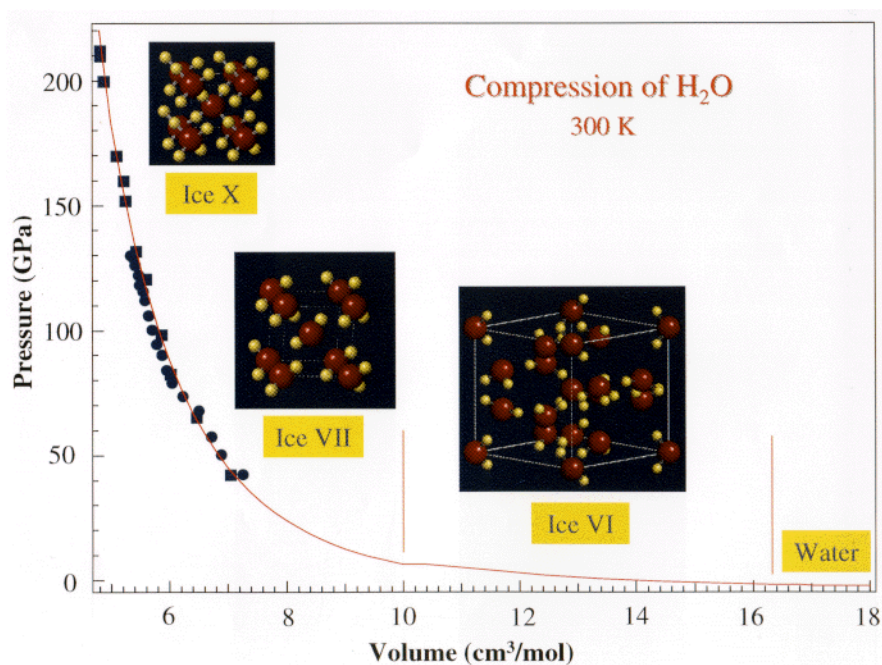

Figure 5. Pressure–volume relations for H_2O at 300 K. The data are from synchrotron x-ray diffraction measurements: circles, reference [20]; squares, reference [19]. Ices VI and VII both exhibit proton (or orientational) disorder, whereas extensive tunnelling is associated with the transition between ices VII and X.
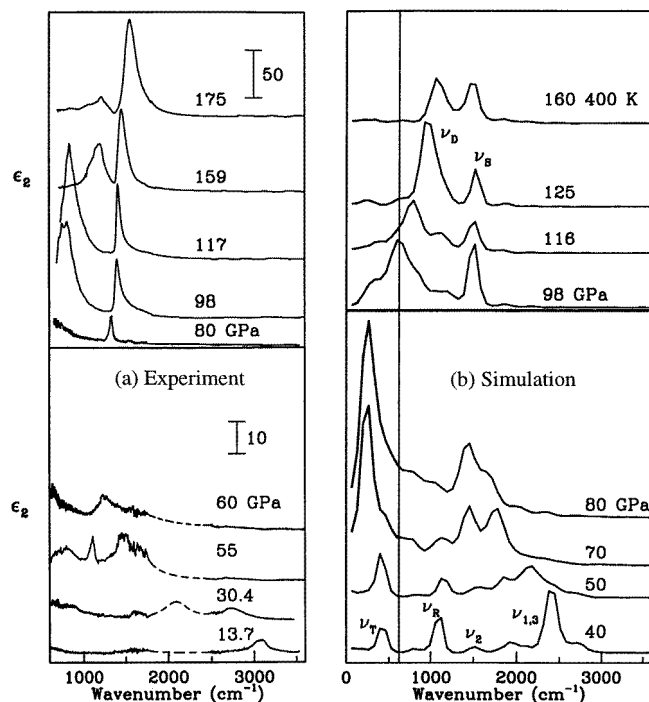
Figure 6. The imaginary part of the dielectric function, ϵ_2, obtained from the infrared reflectivity of ice VII and X. (a) Experimental results obtained by Goncharov *et al* [18]. Data at 55, 60 and 80 K; all others at 295 K. (b) The theoretical calculation of Bernasconi *et al* [21] at 300 K (same scale). The highest-pressure simulation was performed at 400 K.

are in excellent agreement with simulations of the spectra from first-principles techniques (figure 6(b)) [21]. The latter has predicted an intense low-frequency peak outside the range of our measurements, in agreement with the Kramers–Kronig analysis of the experimental data [18].

The synchrotron infrared measurements indicated that major changes occur at 60 GPa [18, 22]. The results are consistent with conventional infrared absorption measurements carried out to 110 GPa [23]. Effective-potential calculations, however, suggest that the formation of a quasi-static, symmetrical hydrogen-bonded state does not occur until higher pressures are reached, perhaps above 140 GPa. In fact, this may be responsible for the changes in relative intensities of the infrared bands at higher pressures (i.e., 150–160 GPa), as pointed out in reference [18]. These changes can be understood from effective potentials for the hydrogen atom between two oxygens (figure 7). We use a double Morse potential with parameters fitted to the equation of state and other data. At lower pressures, the barrier is sufficiently high that tunnel splitting is weak and little proton density is found at the mid-point. With increasing pressure, the barrier decreases, there is increased splitting, and the proton wavefunction (probability density) becomes more diffuse—that is, proton density develops at the mid-point beyond the classical turning point. In this model, the barrier in the effective one-particle potential still exists at 60 GPa, and the proton density is likely to remain diffuse over a broad range of pressures prior to the formation of the quasi-static ('classical'), symmetric hydrogen bonds. This picture is largely compatible with recent simulations of the transition [21, 24].
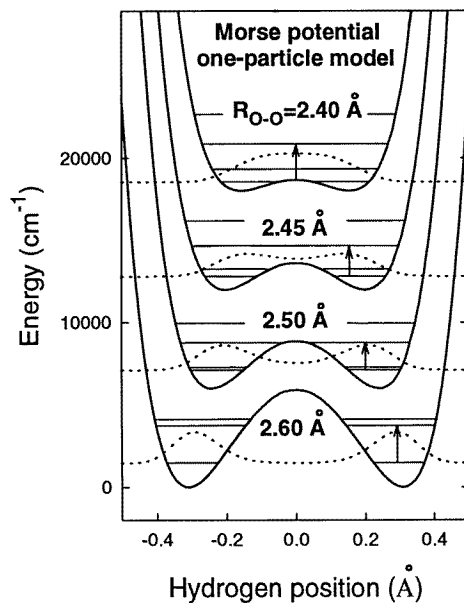
Figure 7. The model based on an effective double Morse potential for the symmetrization of H_2O-ice showing the development of proton density at the mid-point prior to the loss of the barrier [25]. $R_{O-O} = 2.40$ Å corresponds to the pressure at which major changes in the infrared spectra occur.

This intermediate regime between ice VII and X has been the subject of recent experimental and theoretical study [21, 22, 24]. Examination of the absorption and reflectivity vibrational spectra just below the transition reveals a complex sequence of couplings between the soft mode and combination levels having weak pressure dependencies. Using a molecular picture these can be viewed as Fermi resonances—anharmonic interactions that mix the bare harmonic modes. We have recently obtained Raman spectra in the vicinity of the transition [25] in order to understand the complex behaviour associated with the strong anharmonicity, disorder, and tunnelling in the system [18, 22]. Raman spectra of ice at high pressure are very weak and previously have been of no practical value in this range of pressures. However, much more information from Raman spectra can be obtained from measurements with synthetic diamonds, as in the recent H_2 experiments [11]. As in the infrared spectra [18, 22], a large negative shift in the OH stretching mode that results in extensive resonances with other excitations is observed. A new set of weak Raman bands are observed in the high-pressure phase from 60 to 80 GPa [25]. These bands may correspond to excitations predicted by the simple one-particle potential, as shown in figure 7.

5. Van der Waals compounds

Another example of new physical states under extreme conditions is found in molecular alloys, also called van der Waals compounds, that have been found to be stable under pressure. A growing number of examples of this new class of materials have been documented. The CH_4–H_2 binary has an extremely rich phase diagram and shows numerous intriguing phenomena at pressures of 7–60 GPa [26, 27]. Four new solid compounds having
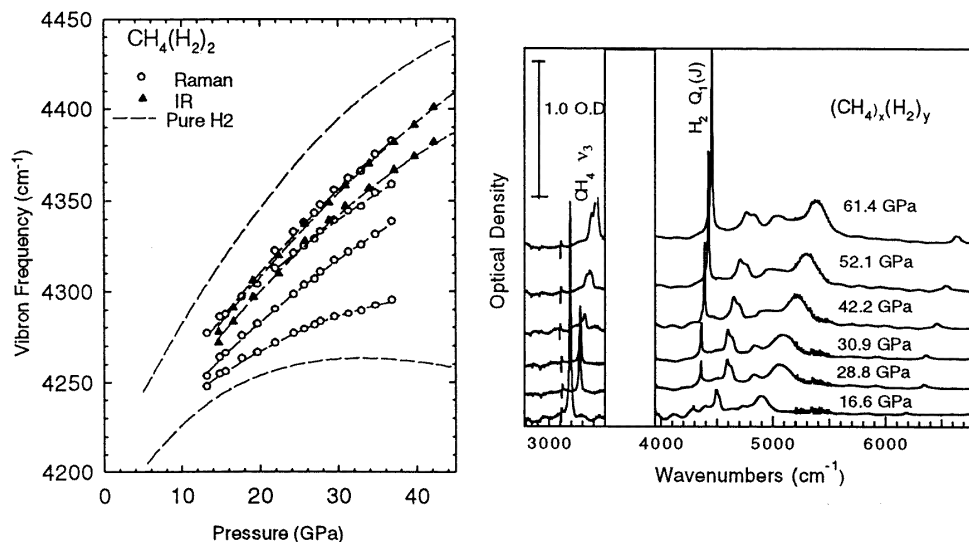
Figure 8. Vibrational spectroscopy of CH$_4$–H$_2$ van der Waals compounds. Left: the pressure dependence of the Raman and infrared H$_2$ vibron (intramolecular stretching mode) in the CH$_4$(H$_2$)$_2$ compound. At higher pressures, the compound transforms and/or changes stoichiometry. Right: synchrotron infrared absorption spectra to higher pressure through the transition and showing the intensity switching of the C–H stretching mode and H$_2$ vibron in the structure [27].

H$_2$:CH$_4$ molar ratios of 1:2, 1:1, 2:1, and 4:1 were discovered and characterized [26]. One of these is a Laves phase with stoichiometry CH$_4$(H$_2$)$_2$, which was found to be stable at 5.6–7.2 GPa, with possible changes in stoichiometry at higher pressures [27]. In addition, infrared measurements provide evidence for charge-transfer processes in the compound at pressures above 30 GPa, where an unusual intensity switching between the C–H stretching and H$_2$ vibron modes is observed (figure 8). It has also been established that substitution of CH$_4$ for Ar gives another stable compound Ar(H$_2$)$_2$, also with the Laves phase structure. Recent Raman measurements at pressures up to 40 GPa of Ar(H$_2$)$_2$ and CH$_4$(H$_2$)$_2$ reveal a rich hydrogen vibron spectra arising from site and vibrational (Davydov) splittings [28]. The CH$_4$ compound (in contrast to that containing Ar) reveals substantial site splitting, which we explain by the anisotropic nature of the crystal field produced by methane molecules. Infrared measurements of Ar(H$_2$)$_2$ to 220 GPa show that the H$_2$ molecules are stable to at least these pressures within the compound [29].

Under low-pressure conditions, water molecules form clathrate hydrates, which consist of networks of cages containing guest molecules. They are unstable at moderate pressures as the open networks break down under compression. In a high-pressure study of the H$_2$–H$_2$O binary system, a novel type of clathrate with a ratio 1:1 was discovered [30]. In this high-pressure clathrate, H$_2$O and H$_2$ form two interlocking diamond networks. With the efficient molecular packing afforded by this structure, the compound (perhaps in a distorted structure) is stable to at least 60 GPa. The vibrational spectrum shows that the compound approaches a symmetrically hydrogen-bonded state near 30 GPa—that is, at lower pressures than in pure H$_2$O (as described above) [32]. This has been confirmed by synchrotron infrared spectroscopy. Stevenson [31] speculated that H$_2$O may accommodate a number of different components at high pressure. Examining binary systems containing water and

other simple molecular species at these and higher pressures is particularly important for planetary science.

6. Superconductivity in compressed sulphur

There have been a series of recent developments in the study of electronic and magnetic order/disorder in low-Z materials, including elemental solids, under pressure. A high-sensitivity magnetic susceptibility technique has been developed to examine super-conductivity at megabar pressures. It involves quenching the Meissner effect by oscillating a magnetic field through the sample's critical field and measuring the magnetization of the sample by phase-sensitive detection techniques. The method has been tested on a variety of materials, including the 1223 high-T_c cuprate [33]. The technique was first extended into the megabar pressure range in a study of Nb to 140 GPa [34].

Superconductivity in the heavier chalcogenides (e.g., Se and Te) under pressure has been the subject of several previous studies [35]. Recently, there has been interest in the lighter members of this family of elements. Under ambient conditions, sulphur forms a molecular solid consisting of eight-membered rings. Evidence for metallization of elemental sulphur at 90 GPa was reported on the basis of optical measurements [36]. Subsequently, theory predicted that sulphur should become a superconductor in its higher-pressure bcc metallic form, predicted to the stable above 550 GPa [37]. We applied the new magnetic susceptibility technique to examine sulphur at megabar pressures. At 93 GPa, a peak in the magnetic response develops which becomes stronger and shifts to higher temperature with pressure [38]. The results are plotted as a function of pressure in figure 9, along with the data for Se and Te. Sulphur transforms directly from an insulator to a 10 K superconductor. T_c increases to 14 K within the bco phase. It then jumps to 17 K at the known transition to the β-Po-structured phase [40]. The onset of superconductivity was also observed in resistance measurements by Kometani *et al* [41], in general agreement with the results of the magnetic susceptibility experiments. Interestingly, the results also confirm the early (and controversial) diamond indentor experiments carried out some twenty years ago [42]; although a convincing estimation of the pressure was not possible in those experiments, their conclusions about T_c are largely confirmed. Very recently, superconductivity in oxygen has been reported near 100 GPa, with T_c equal to 0.6 K [43]. The low value of T_c (figure 9) presumably arises from magnetic interactions in oxygen. The markedly different values for T_c for the chalcogenides, including their different pressure dependences, indicate that different factors control the superconductivity in this family of elements.

7. Conclusions

Significant progress is being made by means of static ultrahigh-pressure techniques in the quest to uncover new physical phenomena under extreme conditions. Examples can be found from recent studies of low-Z materials performed using new diamond-cell techniques. These phenomena range from intriguing behaviour associated with dense molecular hydrogen, quantum effects in hydrogen and hydrogen-bearing systems, pressure-induced interactions in simple molecular mixtures, and the observation of novel superconductors such as highly compressed sulphur and oxygen. The numerous new findings now provide crucial tests of condensed-matter theory.
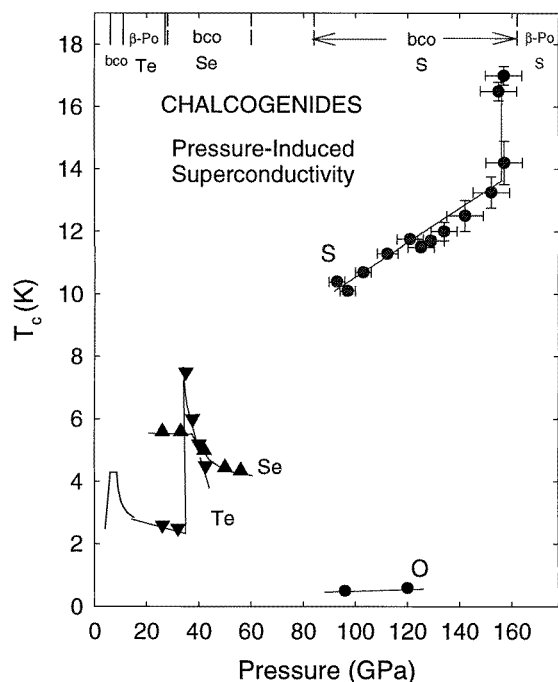
Figure 9. The pressure dependence of the superconducting T_c for the chalcogenides: tellurium and selenium [35], sulphur [38], and oxygen [43]. The ranges of stability of the crystal structures for the different phases are indicated at the top of the figure (after [39]).

Acknowledgments

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