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Molecular character of the metallic high-pressure phase of oxygen

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We report Raman measurements of solid oxygen under high static pressures up to 134 GPa through the transition to the metallic phase. Contrary to previous studies, we observed a moderate decrease in intensity of the Raman vibron at the transition, which allows us to characterize unambiguously the metallic phase as a molecular solid. The transition involves a change in lattice of molecular centers and a possible reorientation of the molecules together with a relatively weak change in molecular bonding. We observed a large pressure range of phase coexistence and hysteresis of the transformation.

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Among diatomic systems solid oxygen stands apart due to its peculiar magnetic interactions, being the only magnetic insulator among elements.[1] Unlike nitrogen and hydrogen, which are expected to undergo insulator-metal transition at pressures above 300 GPa,[2–4] oxygen becomes a metal (and superconductor) at $\sim$100 GPa.[5,6] This difference arises from the unique electronic structure of the oxygen molecule with two unpaired electrons in the ground state (π^*), which leads to the formation of the unpaired molecules with total spin $S=1$. At low pressures the electronic and structural properties of molecular oxygen (in liquid and solid phases) are determined by magnetic interactions,[7] forming a Mott-Hubbard insulator as a result of strong on-site Coulomb repulsion. With increasing pressure, the magnetic moments are expected to collapse, which would lead to the gap closure. The electronic, vibrational, and structural properties of the high-pressure semiconducting phase ϵ undergoing insulator-metal transition has been investigated using different experimental and theoretical techniques.[7–18] It has been found[8,14] that the phase transformation to ϵ oxygen gives rise to a very strong infrared absorption [similar to that in phase III of H_2 (Ref. 19)] in the vibron region and a modest increase in low-frequency modes. This effect has been interpreted as arising from low-energy charge transfer excitations[7] or formation of O_4 molecules.[14] Unfortunately, at present x-ray-diffraction data for ϵ oxygen[20] do not allow for determination of the exact positions of the atoms, so no preference can be given to the presence of O_4 molecules or the alternative O_2 chain model.[9]

The structure of the metallic higher pressure ζ phase also remains unknown. Although it has been reported to be isostructural to ϵ oxygen,[11] this has been disputed in a more recent study.[17] Attempts to measure the Raman spectrum for this phase resulted in either no signal[12] or a weak and barely observed vibron mode.[17] The discontinuity in vibron frequency (-2.5%) observed in the latter work would signal an abrupt weakening of the intramolecular bonding in ζ-O_2 compared to the semiconducting ϵ phase, despite the fact that no substantial volume change has been reported.[11,17]

Until recently, first-principles calculations were not able to reproduce the properties of the ϵ phase, predicting instead magnetic collapse and a concomitant transition to the metallic molecular ζ phase.[13] A recent density-functional theory calculation[18] gives a description of the ϵ phase as a chainlike structure similar to that proposed in Ref. 9. Although experimental data and theoretical calculations imply the molecular character of the ζ phase, the available experimental data are too poor to be considered as solid evidence. The arguments about continuity of the x-ray data through the transition[11] are not satisfactory because no structural refinement was performed. Moreover, existing powder and single-crystal x-ray-diffraction data[11,17] are difficult to reconcile, and the indexing of the ϵ and ζ phases is a matter of continuing debate.[13,17]

Raman spectroscopy has been shown to be essential for characterizing high-pressure phase especially in the case of microscopic amounts of material used in megabar pressure experiments. The presence (or absence) of well-defined high frequency excitations corresponding to internal stretching vibrations (vibrons) can be used as a diagnostic of the nature of phases in question.[21–23] In this paper we present the first detailed Raman data through the ϵ-ζ transition and in the ζ phase. The data show unambiguously that the ϵ-ζ transition is not isostructural, and that the ζ phase is clearly molecular.

We generated pressure with modified Mao-Bell diamond-anvil cells equipped with synthetic ultrapure beveled diamond anvils having 50-μm flats and 150-μm outer culets. Rhenium gaskets were employed to confine oxygen sample (better than 99.99% purity with the natural isotope abundance). The sample was loaded cryogenically through a cold trap in a sealed cylinder; no other material (small grains of ruby for pressure measurements) was present in the high-pressure chamber (cf. Ref. 17). No sign of impurities (e.g., nitrogen) was found by direct careful Raman measurements at low pressure (about 4 GPa). An angular scattering geometry[24] was mostly used to reduce background and avoid overheating of the sample (see Ref. 16). The latter was easily achieved by increased laser spot size (about 15 μm) which reduces the power density compared with standard backscattering geometry. The laser power on the sample was kept below 30 mW. The experiment was performed at room temperature except for one excursion to low temperatures (40–60 GPa, 80 K), which shows little difference compared to room-temperature data. Our Raman setup is described in detail in Ref. 24.

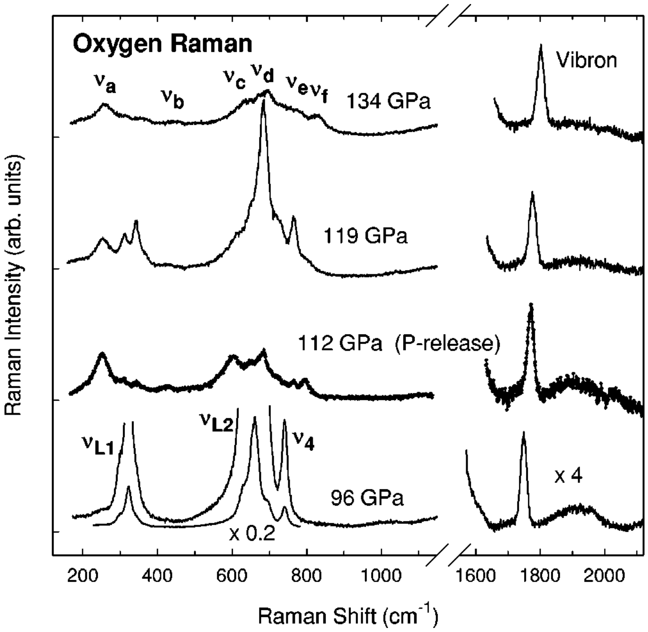

FIG. 1. Raman spectra of oxygen through the ϵ-ζ phase transition. Raman bands of ϵ-oxygen are labeled according to Ref. 12. The solid lines are the spectra taken on pressure increase; the solid line with data points is the spectrum taken on pressure release. The spectra are shifted vertically for clarity.

Figure 1 shows representative Raman spectra through the transition to the ζ phase. Our Raman spectra in ϵ oxygen are essentially in agreement with previous studies.[12] Above 96 GPa new low-frequency Raman bands ν_{a-f} become visible, while those related to ϵ oxygen [dominating bands are ν_{L1} and ν_{L2} (Ref. 12)] lose their intensity with pressure rapidly. At 134 GPa (highest pressure reached) the low-frequency excitations of ϵ oxygen are almost completely supplanted by new bands, which we attribute to the high-pressure ζ phase. The changes in vibrational spectra are accompanied by a gradual change in visible reflectivity, in agreement with earlier observations.[5]

Figure 2 shows the pressure dependence of the low-frequency modes in the transition region. Measurements on pressure release show that the observed spectral changes are reversible (Figs. 1 and 2), but exhibit hysteresis in terms of the relative intensities (Fig. 3). The effect of hysteresis on intensity can also be seen in Fig. 1 by comparing the spectra taken at 112 GPa (taken on decompression) and 119 GPa (taken on compression). These resemble closely the spectra of the ζ and ϵ phases, respectively, despite the fact that the former spectrum is taken at lower pressures.

Unlike the low-frequency spectra, the vibron spectra show no visible changes through the transition (Fig. 1; cf. Ref. 17). The pressure dependence of the vibron frequency is shown in Fig. 4. Below ~100 GPa, our data are in reasonable agreement with previous measurements.[12,17] Somewhat lower frequencies in our experiment (at the same pressure) may be explained by different stress conditions compared to those in Ref. 17 and/or possible effect of local heating.[16] Above 96 GPa, the slope of the vibron frequency shows the kink that was reversibly reproduced on pressure release (Fig. 4).

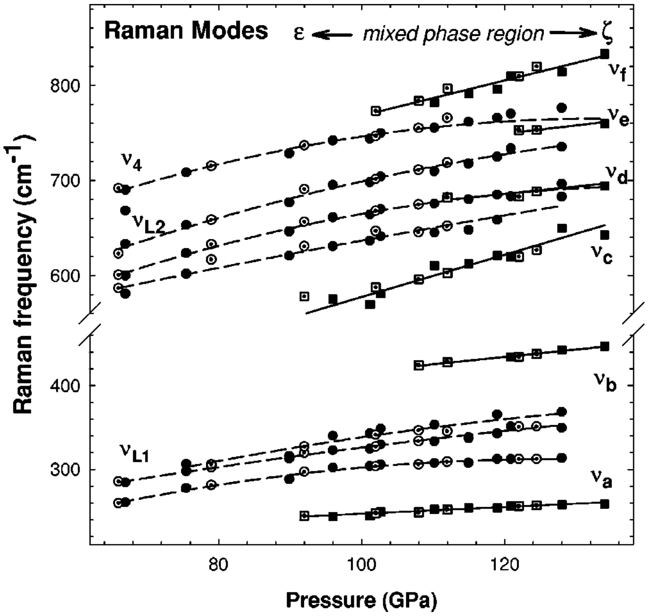

FIG. 2. Raman frequencies of oxygen as a function of pressure obtained by fitting of pseudo-Voigt functions to the measured spectra. Solid and dotted open symbols correspond to pressure increase and decrease, respectively. Circles and dashed lines represent the ϵ phase bands; squares and solid lines represent the ζ phase bands. All lines are guides to the eye. The bands are labeled according to Fig. 1.

The data presented here clearly indicate that phase transition at 90–120 GPa is structural (i.e., first order) A complete interpretation of this transformation requires a more detailed interpretation of the Raman spectra of ϵ oxygen, which is currently missing. According to Ref. 16, the low-frequency Raman spectra correspond to the O_4 molecule fundamentals

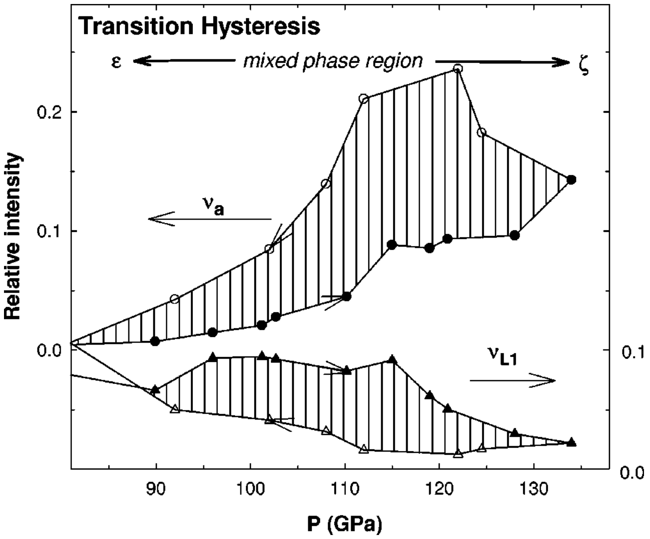

FIG. 3. Pressure dependence of Raman intensities of selected bands of the ϵ and ζ phases (labeled according to Fig. 1). Full symbols denote pressure increase; open symbols denote pressure decrease. Dashed areas correspond to the observed pressure hysteresis.

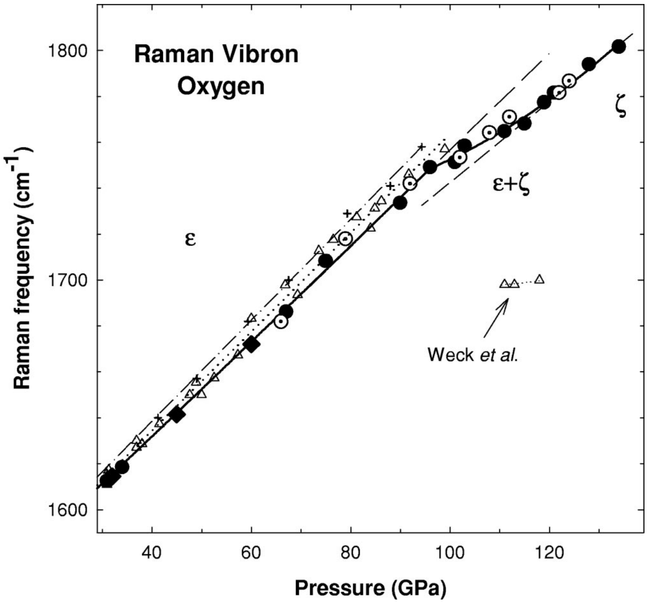

FIG. 4. Pressure dependence of the Raman vibron frequency. Solid and dotted large symbols correspond to pressure increase and decrease, respectively. Circles show room-temperature, and diamonds 80 K data. The thick solid line is a guide to the eye; the long dashed lines are extrapolations of the low-pressure and high-pressure data. Triangles and dotted lines (guide to the eye) are from Ref. 17; crosses and dash-dot lines are from Ref. 12.

(two modes of A_g and B_{1g} symmetries). The number of experimentally observed modes (Figs. 1 and 2) clearly exceeds this prediction and also that for the theoretically proposed $Cmcm$ herring-bone-type structure.[18] Although we cannot confirm or rule out the existence of O_4 molecules, it is clear that a satisfactory crystal model should include at least four O_2 units in the primitive unit cell. Irrespective of whether O_4 model is correct or not, the low-frequency Raman modes represent vibrations related to weaker (compared to the O-O shortest bond) O_2-O_2. This is confirmed by their larger pressure coefficient,[10] which is typical for molecular crystals.

At the transition, the low-frequency modes experience a sudden frequency discontinuity with the exceptions of the ν_{L2} and ν_4 modes, which are difficult to follow, because the ν_d and ν_e modes of the ζ phase are too close in frequency. We interpret these changes to be the result of a rearrangement of the lattice of molecular centers and (possibly) a change in orientational order. The number of the low-frequency Raman modes (six Raman bands, some of which can be an unresolved superposition of two or more modes) suggests a rather complex crystal structure for the ζ phase which preferably contains more than two O_2 units in the unit-cell broadly consistent with the previous x-ray structure determination.[11,17] Alternatively, one would need to invoke a deformation or a disruption of O_4 molecules at the transition to explain the discontinuity in the low-frequency Raman excitations. The behavior of the vibron through the transformation (Fig. 4) is consistent with the first interpretation, because one expects lower vibron frequencies for the O_4 molecules,[16] which contradicts the negative vibron discontinuity at the transition. We estimate that the maximum discontinuity in the vibron frequencies less than $\sim 1\%$ discontinuity at the transition (cf. 2.5% in Ref. 17). Because of coexistence of the two phases in the 96–130 GPa pressure range and the presence of pressure gradients, this behavior is smeared out, so only one vibron peak is observed through the transition region. In fact, the measured linewidth full width of half maximum in this range is about 30 cm^{-1}, compared to the 20-cm^{-1} discontinuity measured as an offset between the linearly extrapolated lower pressure data and the ζ-phase vibron frequency. The persistence of the O-O vibron in the ζ phase clearly demonstrate that this phase is molecular. The vibron frequency change at the transition reflects possible changes in bond length and electron-phonon coupling at the transition. Indeed the frequencies and intensity of the Raman modes in metallic (and superconducting) phase can be renormalized by the electron-phonon coupling.

Finally, we discuss the origin of the difference between the data presented in this work and those from previous experiments.[12,17] The experimental conditions in our experiment and those described in Ref. 12 are similar. Use of advanced Raman techniques (i.e., with holographic optics) and synthetic low-fluorescence diamonds allowed us to improve the signal-to-noise ratio and consequently obtain the Raman spectra of the metallic ζ phase. It also allowed us to show that the intensity of the vibron band decreases moderately and stays relatively high up to the highest pressures reached. Unlike the authors of Ref. 17, who used a Ne-O_2 mixture to maximize "the Raman part of the spectra," we did not observe the abrupt discontinuity in the vibron frequency. Although the origin of the extra Raman peak at ~ 1700 cm^{-1} reported in Ref. 17 is not clear, we speculate that it may be related to the presence of Ne (up to 90 vol %) in the sample. Together with the large amount, of new low-frequency excitation, the new vibron measurements provide a basis for further understanding the molecular phase of oxygen.

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