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## Solid Oxygen at High Pressure and Low Temperature: Raman Observation of Librons and Vibron

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This paper reports the results of an experimental high-pressure study of solid oxygen at low temperature up to 60 kbar. Librons and vibron were observed with Raman light scattering. Evidence is presented for a low-temperature phase transition at about 9 kbar. Very recently a phase transition was predicted in this temperature and pressure regime. However, the overall agreement with theory is modest.

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Solid oxygen is a unique molecular solid due to the presence of two unpaired electron spins on each molecule. The interplay of the spin-independent and the exchange interactions introduces the possibility of a rich phase diagram. One of the consequences is that the low-temperature  $\alpha$  phase is the only known insulating single-element antiferromagnet. Many experiments were performed, especially in the 1960's, but the uncertainty about the influence and magnitude of the magnetic interactions prohibited in many cases a consistent interpretation.<sup>1</sup> However, recently, as a result of measurements of magnetization under pressure<sup>2</sup> and neutron scattering experiments,<sup>3,4</sup> a coherent and consistent picture of the magnetic excitations seems to emerge. Although there still remains some uncertainty about the exact nature of the interactions between two oxygen molecules, the main features are sufficiently known by now to provide a basis for realistic calculations. Helmy, Kobashi, and Etters<sup>5</sup> have already performed extensive calculations of the pressure dependence of thermodynamic properties and excitation frequencies of solid oxygen at low temperature using the latest ideas about the interactions. The experimental determination of these properties would be a very severe test for these, and other, new ideas. An interesting result of the work of Helmy, Kobashi, and Etters is that they predict the existence of a new low-temperature phase transition.

We have performed an extensive study of the low-energy excitations of solid oxygen by Raman light scattering at low temperature. All previous high-pressure studies have been performed at high temperature.<sup>6,7</sup> The predicted low-temperature phase transition, which became known to us during this experiment, would not involve an enlarging of the unit cell. As a consequence no splitting of lines would be present. Such a phase transition could

manifest itself as a change in slope of the plots of excitation energies against pressure, and this of course would require many data points to be convincing.

Samples of oxygen (Matheson Research Grade, purity > 99.999%) were condensed into the intermediate-temperature  $\beta$  phase in a diamond anvil cell<sup>8</sup>; the sample was annealed in the high-temperature  $\tau$  phase and then cooled down slowly. The initial sample size (at zero pressure) was approximately 100  $\mu\text{m}$  in diameter as well as in thickness. The pressure was determined from the shift of the luminescence spectrum of a ruby chip enclosed in the sample.<sup>9</sup> About 200 mW of the 514.5-nm line of an argon-ion laser was used as the light source for both the Raman scattering (180° backscattering geometry) as well as the ruby luminescence.

The Raman spectrum of solid oxygen has three well defined features at low pressure: the vibron, which is a collective  $k=0$  excitation of the intramolecular vibration, a libron, and a band at approximately twice the energy of the single libron which we will refer to as the  $D$  band. We have studied these three features in various runs at 6 K and at 18 K for pressures up to 60 kbar. We could observe the  $D$  band up to 35 kbar. Because of extreme broadening observation was not possible at higher pressure. The linewidth of the libron band increases from 3  $\text{cm}^{-1}$  at zero pressure up to  $\approx 12 \text{ cm}^{-1}$  at 50 kbar, whereas the vibron has a width of less than 2  $\text{cm}^{-1}$ . An orange-red color appeared at about 45 kbar and became stronger when pressure was increased.

Our experimental results are presented in Fig. 1. We could not see any appreciable difference between the 6-K and the 18-K data. These results are the compilation of several independent runs. Each run was started at low pressure. Since a small

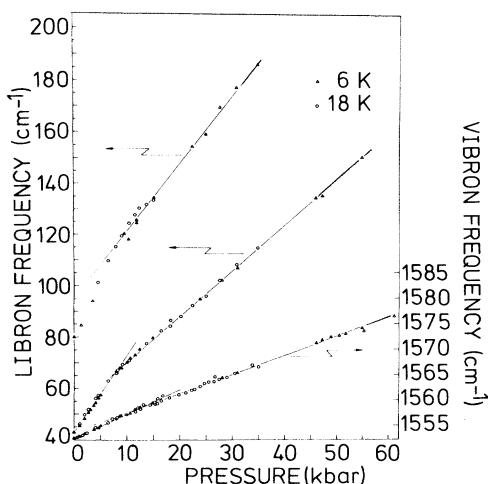


FIG. 1. Vibron frequencies (lower curve), libron frequencies, and  $D$ -band frequencies (upper curve) as a function of pressure at 6 K and at 18 K. Solid lines are piecewise linear fits.

hysteresis was observed on release to zero pressure, each run was started by annealing the sample in the  $\beta$  phase. It is remarkable that both the libron and vibron frequencies can be very well represented by two straight lines. These two lines cross at  $8 \pm 1$  kbar for the librions and at  $11 \pm 3$  kbar for the vibrons. This sudden change of slope indicates that a phase transition occurs at this point. Since no splitting of the bands was observed, we conclude that the unit cell is not enlarged.

Helmy, Kobashi, and Etters<sup>5</sup> have calculated the libron frequencies and vibron frequency shifts as a function of pressure. Their results as well as the fits to our experimental data are depicted in Fig. 2. Since Helmy, Kobashi, and Etters have not given the absolute magnitude of the vibron frequency we have calibrated their results with our experimental zero-pressure data. In principle two libron modes are Raman active, viz. a libration around the crystallographic  $a$  axis ( $L_a$ ) of the monoclinic unit cell and a libration around the crystallographic  $b$  axis ( $L_b$ ). In all theories these two librions are almost degenerate at  $k=0$ , and experimentally only one line is observed. The character of the much broader  $D$  band is not established yet, although a two-libron transition is a likely candidate.

The absolute agreement between theory and experiment is only modest. It should be pointed out that Helmy, Kobashi, and Etters<sup>5</sup> realized that there are still some uncertainties left with respect to the intermolecular potential, and these could well be responsible for the differences. In contrast to their theory the experimental data clearly show a linear

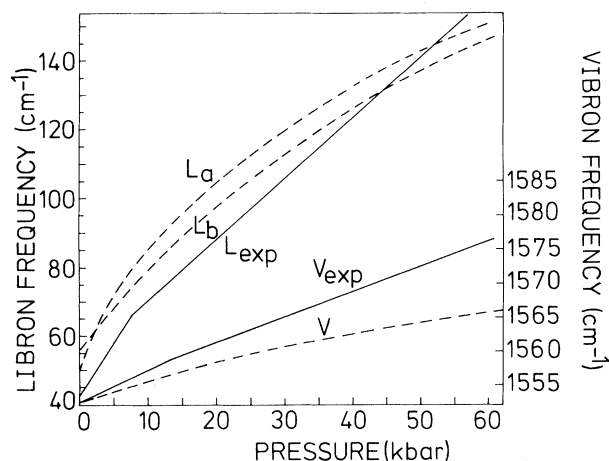


FIG. 2. Comparison between theory (from Ref. 5) and present experiments of libron and vibron frequencies. Solid lines are the piecewise linear fits to our experimental data and dashed lines are the theoretical results.

behavior up to high pressure. They predict a phase transition at 6 kbar from a monoclinic to an orthorhombic structure at low temperature, and they conclude from their theory that the transition is not first order.<sup>5</sup> From our experiments the phase transition seems to be of (weakly) first-order character. The first-order character of a phase transition is always a subtle point, from both the experimental and the theoretical side. In an experimental situation the continuous change might be so steep that it appears to be of first order. In a theoretical analysis a phase transition of second-order character can easily become first order by introduction of a coupling of the order parameter to another field. It is clear that more experiments and new calculations are necessary to unravel the nature of the low-temperature phase transition.

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<sup>1</sup>See G. C. DeFotis, Phys. Rev. B 23, 4714 (1981), and

references therein.

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<sup>8</sup>The design of this diamond cell was developed by Silvera and Wijngaarden. See for instance I. F. Silvera and R. J. Wijngaarden, *Phys. Rev. Lett.* **47**, 39 (1981).

<sup>9</sup>G. J. Piermarini and S. Block, *Rev. Sci. Instrum.* **46**, 973 (1975).