PHYSICAL REVIEW B VOLUME 60, NUMBER 9 1 SEPTEMBER 1999-I

# High-pressure and low-temperature infrared study of solid oxygen: Evidence of a new crystal structure

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(Received 22 January 1999; revised manuscript received 10 March 1999)

Infrared spectroscopy has been applied to the study of solid oxygen at high pressure and low temperature. An absorption line in the vibron fundamental mode region has been observed, and its behavior with pressure measured up to the transition to the $\epsilon$ phase. This absorption, not expected according to the symmetry of the $\delta$ phase, indicates the existence of a new crystal structure between 2 and 8 GPa at low temperature. The comparison of the infrared and Raman frequency evolution with pressure is done quantitatively on the basis of a simple vibrational coupling model and the intermolecular coupling force constant is obtained. In contrast to solid hydrogen, here the coupling constant is positive and shows a strong dependence on the intermolecular distance which can indicate that significant charge transfer processes are already present in this low-pressure phase. [S0163-1829(99)05533-2]

A renewed interest in the properties of oxygen at high pressure has arisen again after its metallization at 96 GPa has been demonstrated.[1] However, many aspects of the physics of this system remain to be interpreted in a satisfactory manner. The phase diagram at low temperature is not known, even if it is commonly accepted that the magnetic properties determine the parallel alignment of the molecules in all the low temperature crystal phases.[2,3] Furthermore, the visible absorption (orange or red color) observed in the $\delta$ and $\epsilon$ phases[4] testifies, already at low values of pressure, for big changes in the electronic properties, that are not clearly understood. The intermolecular potential is affected severely by electronic properties. Because of this, infrared and Raman data, able to reveal fine changes in the internal and external vibrational properties, are particularly relevant. In this paper we present the results of a low temperature (25–50 K) infrared absorption study between 1 and 8 GPa. A narrow, unexpected infrared peak is detected in the fundamental vibrational mode region. This observation contrasts with the assignment of this part of the $P-T$ diagram to the orthorhombic $\delta$ phase.

A membrane diamond anvil cell equipped with type IIa diamonds and an inconel gasket was loaded with $O_2$ (purity $>99.99\%$) by means of cryogenic loading equipment. The infrared experimental apparatus, with specific attention to the low temperature application, has been carefully described elsewhere.[5] The pressure is determined from the peak wavelength of the $R1$ ruby fluorescence band. The instrumental resolution used was better than 0.5 $\mathrm{cm}^{-1}$ in all the measurements.

Oxygen was crystallized in the $\beta$ phase by pressurizing the fluid at 5.5 GPa around 315 K. The crystal was annealed and then cooled avoiding the $\gamma-\beta$ phase transition where a strong decrease in volume (5.4%) takes place.[6] The spectrum in the fundamental vibration region was monitored during all the process, but, as expected from symmetry arguments, no measurable absorption has been detected in the $\beta$ phase. Spectra were collected, on different samples, during an isobaric cooling at 4 GPa from 150 to 23 K, therefore crossing the $\beta-\delta$ boundary at about 140 K, and during isothermal scans at low temperature (23 K and 50 K) from 0.9 GPa to the $\delta-\epsilon$ phase transition (7–8 GPa). On cooling at 4 GPa, a broad absorption band, extending approximately from 1595 up to 1725 $\mathrm{cm}^{-1}$, appears below 135 K, in correspondence of a predicted phase change.[7] The intensity of this feature markedly increases as the temperature is further lowered, and becomes more structured below 77 K, where three maxima can be identified at about 1680, 1695, and 1715 $\mathrm{cm}^{-1}$. In the fundamental vibration region a very weak line, whose intensity increases as the temperature is lowered, begins to be visible in the 95 K absorbance spectrum at 1549 $\mathrm{cm}^{-1}$. Since at this pressure the Raman vibron peak is observed at 1569 $\mathrm{cm}^{-1}$ (80 K),[8] the weak line at 1549 $\mathrm{cm}^{-1}$ cannot be attributed to the Raman component of the fundamental mode whose infrared intensity is induced by defects or impurities. Furthermore the narrow bandwidth, 2–3 $\mathrm{cm}^{-1}$ between 2 and 7 GPa, and the almost Lorentzian line shape testify a good crystal quality. The unit cell of $\delta$ oxygen is orthorhombic face centred ($Fmmm$, $D_{2h}^{23}$) with four molecules

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TABLE I. Correlation diagram among molecular, site and factor group symmetry of the *Fmmm* structure of the $\delta$ phase.

| Mode | Molecule<br>$D_{\infty h}$ | Site<br>$D_{2h}$ | Factor group<br>$D_{2h}$ |
|---|---|---|---|
| $(O-O)$ | $\Sigma_g^+$ | $A_g$ | $A_g$ |
| $(T_z)$ | $\Sigma_u^+$ | $B_{1u}$ | $B_{1u}$ [a] |
| $(T_x,T_y)$ | $\Pi_u$ | $B_{2u}+B_{3u}$ | $B_{2u}+B_{3u}$ [a] |
| $(R_x,R_y)$ | $\Pi_g$ | $B_{2g}+B_{3g}$ | $B_{2g}+B_{3g}$ [b] |

[a] Acoustic mode.

[b] Librational mode.

aligned parallel.[9] The center of mass of the molecules lies on sites having $D_{2h}$ symmetry, i.e., only one molecule is contained in the primitive cell, therefore no Davydov splitting of the fundamental mode is expected. In Table I the correlation between the isolated molecule and the factor group symmetries is presented. It results that only one Raman active ($A_g$) component should be observed, therefore we explain the splitting of the fundamental mode on the basis of a different crystal structure. Finally, the broad absorption above 1600 $\mathrm{cm}^{-1}$ is correlated to phonon side band, i.e., vibron + lattice phonon double excitations. Two lines, assigned as libron excitations, were indeed observed by Raman scattering[8] at about 126 and 194 $\mathrm{cm}^{-1}$ (4–5 GPa).

During the isothermal compression, the infrared line is observable above $\simeq 2$ GPa, and its intensity rapidly grows with pressure. Some spectra of the series measured at 23 K are shown in Fig. 1. The position of this peak is not much affected by the pressure increase and the overall change in frequency between 2 and 7 GPa is 0.15 $\mathrm{cm}^{-1}$. At about 7.5 GPa another broader peak appears in the spectrum, and it is ascribed to the formation of the $\epsilon$ phase (monoclinic $A2/m$; $z=8$).[10] A strong infrared absorption is indeed reported in this phase also at room temperature.[2,11] The coexistence of the two phases is evident up to 8 GPa, where the intensity of the symmetry allowed $\epsilon$ mode is enormously increased while the peak of the lower pressure phase is only slightly reduced. The vibron peak in the $\epsilon$ phase appears down shifted of about 15 $\mathrm{cm}^{-1}$ with respect to the one of the low pressure phase. This shift is much larger than that measured for the Raman component at 80 K (about 7 $\mathrm{cm}^{-1}$).[8]

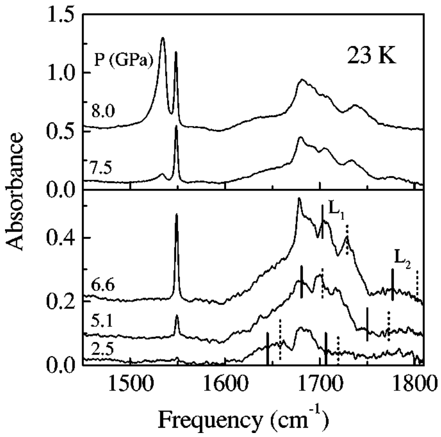

FIG. 1. Low temperature infrared spectra of the vibron region of oxygen before (lower part) and just at (upper part) the transition to the $\epsilon$ phase. The boundaries of the $L_1$ and $L_2$ regions are obtained at each pressure by summing the libron frequencies (Ref. 8) to the infrared (full lines) and to the Raman (dotted lines) vibron frequencies.

The P-T region investigated in this study, assigned to the $\delta$ phase according to Ref. 12, was extensively studied only by Raman spectroscopy. A phase transition around 3 GPa was claimed by Jodl *et al.* at 10 K,[8] but not confirmed by other Raman experiments.[13] Yen and Nicol[7] favor the existence of a phase transition at higher pressure and temperature ($\simeq 5$ GPa and 120 K), but do not observe any effect on the Raman vibron. In this study we do not get any precise indication of phase transitions between 2 and 7.5 GPa even though, during the 23 K isothermal scan, a cusp in the vibron frequency evolution with pressure at about 4.2 GPa could be indicated. At the same pressure Meier *et al.*[13] recorded the appearance of a red-orange coloration of the sample. However, none of these experimental results provide a reliable evidence of the existence of a phase transition.

In our opinion all the pressure range between 2 and 7.5 GPa belongs, below 50 K, to the same crystal structure which is different from that of the $\delta$ phase. Only minor changes, as also evidentiated by the Raman results, should characterize the evolution between the monoclinic structures of the $\alpha$ and $\epsilon$ phases. We favor, therefore, still a monoclinic or an orthorhombic structure where only a doubling, with respect to the $\delta$ or $\alpha$ phases, of the primitive cell takes place. Since the two Davydov components, one infrared and one Raman active, suggest a centrosymmetric cell, with at least two molecules, we restrict the symmetry of the possible factor groups to $C_{2h}$ (monoclinic) or $D_{2h}$ (orthorhombic). The increased number of molecules in the cell should induce the activity of five or more new lattice modes. Even though some of these modes will be Raman active, none of the low temperature experiments reported such changes in the lattice modes region. The infrared experiment seems to be therefore the best approach to obtain information on this phase since high pressure and low temperature x-ray experiments are technically demanding.

Infrared phonon sidebands show a good resemblance to the one phonon density of states (DOS) in simple molecular crystals at low temperature and room pressure.[14] In Fig. 1 the pressure evolution of the structure of the phonon sideband can be clearly discerned. The dispersion in frequency at 4 GPa is approximately twice the one of the zero pressure $\alpha$ phase.[15] We have also shown the frequency regions ($L_1$ and $L_2$) whose lower and upper limits are calculated as the sum of the libron frequencies, according to the values reported in Ref. 8, and the infrared and Raman vibron frequency (full and dotted lines, respectively). Contrary to the $L_1$ region, which always falls within the one phonon density of states, the $L_2$ region always appears to be outside. This suggests that the higher frequency Raman peak could be due to a two-phonon excitation rather than to a second libron.

The dependence on pressure of the infrared and Raman vibron frequencies is reported in Fig. 2. The nearly independence from pressure of the infrared vibron frequency contrasts with the behavior of the Raman component whose energy increases steeply (3 $\mathrm{cm}^{-1}$/GPa).[8] An analogous difference between the infrared vibron band (induced by

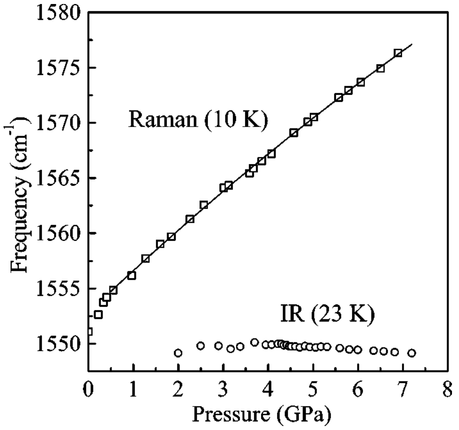

FIG. 2. Frequency evolution of the Raman (squares; Ref. 8) and infrared (circles; this work) vibron components as a function of pressure. The solid line is the best fit used to calculate $\omega_R$ in Eq. (3). The error bars on the infrared data are $\simeq 0.1\ \mathrm{cm}^{-1}$ not exceeding therefore the dimension of the symbols.

ortho-$H_2$ impurities) and the Raman vibron has been observed in solid hydrogen, where however it is the Raman band to show the lower frequency, and the relative difference reaches values comparable to those reported here ($\simeq 1.8\%$ of the molecular vibration frequency at 7 GPa) only at much higher pressure (25–30 GPa).[16] This phenomenon has been successfully interpreted as due to vibrational coupling between neighboring molecules, and the relative vibrational coupling constant has been derived quantitatively.[17,18] This result was obtained by extending the original pair interaction model of van Kranendonk[19] to the crystal. In the following a similar quantitative analysis is carried on for solid oxygen in the present experimental situation.

We refer for the notation to Refs. 17 and 18, and we only specify the hypothesis under which the result expressed by Eqs. (2) and (3) is derived, omitting the details of the calculation. The force constant $G$ depends here, besides from the pair separation $R_{ij}$, from the molecular orientation, $\omega_i$ and $\omega_j$, with respect to the intermolecular axis. Even though the exact crystal structure of this new oxygen phase is not known, we assume a layered structure, as it is the case for the $\alpha$, $\delta$, and $\epsilon$ phases, with parallel oxygen molecules in each layer, and we neglect interactions between molecules in different layers. This implies that the dependence of $G$ from $\omega_i$ and $\omega_j$ can be neglected, since these variables have the same values for any molecular pair. For a crystal with two equivalent molecules per primitive cell, the expression of the $2\times 2$ dynamical matrix contains the force constant $G(R)$ calculated for all the pairs of interacting molecules, hence for different values of the distance $R$. Assuming that the functional dependence of $G$ on the intermolecular distance $R$ could be expressed by a power law,

$$G(R)=G_0\left(\frac{R}{R_0}\right)^n, \tag{1}$$

then it results $G(R_{ij})=k_{ij}G(R_0)$, with $R_0$ a typical pressure dependent scale length, and with the proportionality constants $k_{ij}$ independent of pressure, assuming uniform compression in this small pressure range. The quantity $G(R_0)$ can then be factored out in the dinamical matrix, which is straightforwardly solved with the result

$$\omega_{\pm}=\left[\frac{F+(A\pm B)G}{\mu}\right]^{1/2}, \tag{2}$$

where $\mu$ is the reduced mass, $A$ and $B$ are two constants that depend on the particular crystal structure but not on pressure, $\omega_+$ and $\omega_-$ refer to the in- and out-of-phase vibration of the pair, being therefore respectively the Raman and the infrared mode. The value of the coupling constant $G$ can be extracted to within a factor from the experimental frequencies at every pressure, resulting

$$G=\frac{(\omega_R^2-\omega_{IR}^2)\mu}{2B}. \tag{3}$$

At long distance, the force constant $G$ is described by a negative dipole-dipole interaction term proportional to $R_{ij}^{-6}$. For solid hydrogen, Moshary *et al.* found an evolution of $G$ proportional to $R_{ij}^{-7.2}$, up to 100 GPa, explaining this result with a short range correction to the intermolecular interactions.[18] It is a remarkable phenomenon that, as it results immediately from Eq. (3), $G$ is positive for oxygen molecules, while for hydrogen it is negative.[17] It can be demonstrated that for two linear molecules interacting only with long range dispersion forces, the sign of $G$ should be negative, irrespective to the molecular orientation. This result can be derived easily starting from the expression of the interaction energy for linear molecules,[20] and in the hypothesis that both components of the molecular polarizability have a positive derivative with respect to the internuclear distance. Therefore, it is evident that for solid hydrogen the interaction can be described with only a small correction to the long range behavior.

By using the Raman data of Ref. 8 the relative $G$ force constant is then calculated, at any pressure. To report this quantity as a function of the internuclear distance, we have calculated the evolution of the molar volume with pressure by extrapolating up to 7.2 GPa the EOS given in Ref. 21, valid at 50 K up to 2 GPa and successfully tested by the

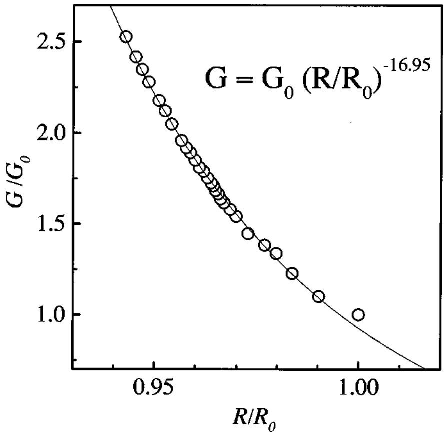

FIG. 3. Vibrational coupling constant $G$ as a function of intermolecular distance. Squares: experimental data from Eq. (3); solid line: best fit according to Eq. (1). The relative error on the $G$ data is $\leqslant 0.2\%$ assuming $1\ \mathrm{cm}^{-1}$ of uncertainty on the Raman vibron position.

same authors up to 5.5 GPa. Our extrapolation up to 7.2 GPa, given the approximations of this analysis, appears to be justified. In Fig. 3 the experimental values of $G/G_0$ are reported, as a function of the scaled intermolecular distance $R/R_0$, together with the best fit with a power law function according to Eq. (1). The extremely large exponent value we get from the fit, $n \simeq -17$, even though obtained in a very limited density range, and the positive sign of $G$ can only be explained with a dramatic change of the interaction at short range which can be ascribed to charge transfer processes. A suitable comparison is the low temperature $\epsilon$ phase of solid nitrogen in a overlapping density region. The $\nu_2$ Raman and infrared peaks shift linearly with pressure between 2.5 and 12 GPa (Ref. 22) with almost identical slope values, 2.03 and 2.04 $\mathrm{cm}^{-1}$/GPa for the infrared and Raman components respectively, indicating the complete absence in nitrogen of vibrational coupling even at these high densities. It should be pointed out that in solid nitrogen, at the same density, the distance among nearest-neighbors is larger than in oxygen of something more than 10% (data at 110 K),[23] even though the relative orientations of the molecules makes the distance between closest atoms of nearest-neighbor molecules shorter (2.7–2.8 Å).

In conclusion, we have obtained low-temperature infrared data on the high-pressure phases of solid oxygen. These data will force to reinterpret the structural evolution of solid oxygen, since the presence of infrared activity for the vibron is not explained by the present assumptions on the low-temperature portion of the phase diagram. A quantitative analysis of the intermolecular vibrational coupling discovers a surprisingly large contribution of the short range interactions. This can indicate that charge transfer processes are important also in this pressure range and they must be necessarily considered in the study of the $\epsilon$ phase.

This work has been supported by the European Union under Contract ERB FMGE CT 950017.

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