High-pressure infrared spectroscopy of solid oxygen

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The infrared IR absorption spectra of molecular solid oxygen O_2 have been studied to 92 GPa at room temperature. The IR-active vibron fundamental around 1500 cm^{-1} consisted of at least four absorption bands and their frequencies showed a turnover at 25 GPa with increasing pressure and then monotonically increased to 87 GPa after an initial decrease. The significant increase in the frequencies of the IR- and Raman-active vibrons has suggested a strengthening of the O-O intramolecular bond with pressure. An increase in the frequency difference between the IR and Raman vibrons with a pressure dependence similar to those of librons has also indicated an increase in the O_2-O_2 intermolecular bond. The absorbance saturation over all frequencies in the present observable region above 92 GPa was attributed to the insulator-metal transition due to a discontinuous band-gap closure. The structure of the ε phase has been examined based on the spectroscopic data.

I. INTRODUCTION

Pressure-induced metallization and molecular dissociation of solid oxygen with molecular magnetism have attracted special interest with a view to understanding the fundamental effect of chemical bonding and novel electronic and magnetic properties of the resultant high-pressure phases. Since the first observation of metallization around 95 GPa by Desgreniers, Vohra, and Ruoff,[1] many studies on the properties of solid oxygen beyond 100 GPa have been carried out. Our recent high-pressure x-ray diffraction study[2] has revealed a structural transition from the ε to ζ phase at 96 GPa corresponding to the metallization. In this metallic phase, superconductivity has been discovered at the lower temperature of 0.6 K.[3] A more recent study of *ab initio* molecular-dynamics simulations[4] has reported excellent agreement with these experimental results.

As for the molecular dissociation, the high-pressure behavior of molecular vibrations has been studied by Raman scattering experiments.[5] The frequency of the Raman-active vibron (the intramolecular stretching mode), with increasing pressure, increased with a large positive pressure coefficient while the scattering intensity showed a considerable damping due to a narrowing of the band gap. Around the metallization pressure, the vibron peak merged into the background and became undetectable. This behavior was attributed to an abrupt increase in the absorption coefficient of the light due to the creation of nearly free electrons. Up to now, there has been no positive experimental evidence for the dissociation of O_2 molecules in the structural transition.

The pressure behavior of the molecular bondings in solid oxygen will provide information on the molecular dissociation. In order to discuss the intermolecular and intramolecular interactions in solid oxygen, IR absorption data are indispensable. In this paper, IR absorption experiments have been carried out up to 92 GPa, and the molecular bonding of O_2, the structure of the ε phase, and the insulator-metal transition have been examined based on the obtained IR spectroscopic data together with our previous Raman data.[5]

As for the ε phase, which is stable over a wide pressure range from 10 to about 100 GPa at room temperature, the single crystal analysis by Johnson, Nicol, and Schiferl has proposed the space group of $C2/m$.[6] However, the atomic positional parameters in the monoclinic cell have not been determined. Previous IR absorption studies to 20 GPa (Refs. 7 and 8) have observed a strong absorption due to one IR-active vibron fundamental in the ε phase. The results indicated a strong intermolecular interaction characterized by a charge-transfer excitation in this phase.

II. EXPERIMENT

Merrill-Basset diamond-anvil cells (DAC), which had tungsten carbide backings with a wide optical window of 70° aperture to both sides, were used to accomplish the infrared absorption experiments for solid oxygen in the pressure range from 10 to 100 GPa at room temperature. Udimet700 composed of a $Ni_3(TiAl)$-based heat resistant alloy was used as the metal gasket. Type-IIA diamonds were mainly used as the anvils. The type-IA diamond, which has a much stronger and broader absorption in the range between 1380 and 1070 cm^{-1}, was also used because the IR-active vibron fundamental band of oxygen avoided superposing on the absorption. Pressure was determined by a ruby fluorescence method.[9]

IR spectra in the frequency range from 5000 to 550 cm^{-1} were obtained with a JASCO MFT-2000 micro-optical Fourier-transform spectrometer with a cooled Hg-Cd-Te detector. Typically, 500 scans with 4-cm^{-1} resolution were averaged. Raman scattering and x-ray diffraction measurements were simultaneously carried out at each pressure. Raman spectra were obtained in back-scattering geometry.[5] The experimental details and results of the x-ray diffraction studies will be described elsewhere.

Liquid oxygen of 99.999% purity was loaded into a hole in a metal gasket in the cells at 77 K. In the present paper, six experimental runs for the IR measurement were carried out under different experimental conditions. Three kinds of ε-O_2 samples were prepared with different crystal conditions. One consisted of powder samples and was simply prepared by

compression above 10 GPa at room temperature. The as-prepared powder samples, which showed a strong absorption due to the IR-active vibron fundamental (the absorption peak saturated), were also used for the x-ray diffraction measurement. The powder x-ray pattern of the ε phase at 17 GPa was assigned to a monoclinic cell with lattice constants $a = 7.827$ Å, $b = 5.526$ Å, $c = 3.678$ Å, $\beta = 116.1°$, and $Z = 8$. The values agreed with our previous data[2] and were consistent with those of the previous data at 19.7 GPa.[6] The others were polycrystalline and single-crystal samples, which were grown by a strain-annealing method under high-pressure and high-temperature conditions of about 25 GPa and 650 K. By using the annealed samples, we could observe the detailed features of the absorption due to the IR-active vibron fundamental. Visual observation under a microscope suggested that the polycrystalline samples were an aggregate of the single crystal of 10–30 μm size. The crystal exhibited a remarkable dichromatic character and had several color facets, deep red, red, orange, yellow, and colorless. The single-crystal samples were colorless and had a domain of 70 μm diameter. An x-ray analysis showed that the ab plane of the crystal was almost perpendicular to the culets of the diamond anvils. The molecular axis of O_2 is considered to be mainly perpendicular to the ab plane.[8] For the single crystal, the polarization property of the IR spectra was measured by inserting a metal-grid type polarizer in front of the detector. The optical rotatory power of the diamond anvils under uniaxial stress was tested by measuring the dichroism of a polyethylene film, which was placed on an incident window of a DAC that included the ε-O_2 sample. The loaded diamonds did not linearly polarize the light in the IR region within an accuracy of $\pm 5°$ but slightly did elliptically. The effect of the elliptical polarization was too weak to explain the strong polarization property observed in the ε-O_2 phase as mentioned below.

III. RESULTS

A typical IR spectrum for the ε phase obtained at 26.1 GPa is illustrated in Fig. 1. The frequency region between 1800 and 2400 cm^{-1}, obscured by the absorption due to the diamonds, is excluded. The sample was the strain-annealed polycrystalline and showed absorptions around 1500, 3000, and 4400 cm^{-1}. Insets in the figure illustrate the magnification of the absorption. The strong absorption around 1500 cm^{-1} corresponds to the IR-active vibron fundamental and has an absorbance $\log_{10}(I_0/I)$ of 1.8. The absorption coefficient, $\alpha = \log_{10}(I_0/I)/d$, was calculated to be is 1.2 $\times 10^3$/cm from a sample thickness d of about 15 μm, which was estimated from the thickness of the recovered metal gasket. This value is smaller than the previous value of 1.6 $\times 10^3$/cm.[7] The significant result of this work is the observation of a splitting of the IR-active fundamental. This absorption seems to consist of more than three bands. The absorptions around 3000 and 4400 cm^{-1} are combinations. The former consists of six absorption bands, which are labeled by symbols from C_1 to C_6. The larger number of the combination bands also suggest that the IR vibron fundamental is not a singlet.

The fine structure of the absorption for the IR-active vibron fundamental was recorded at 27 GPa using the single-crystal sample. The absorption exhibits a strong polarization
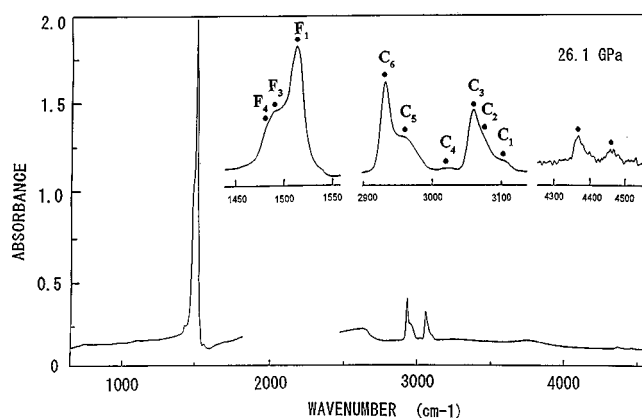

FIG. 1. Typical IR absorption spectrum of the strain-annealed polycrystalline sample of the ε phase at a pressure of 26.1 GPa. Absorption bands have been observed around 1500, 3000, and 4400 cm^{-1}. Insets in the figure show the magnification of the absorption bands. The absorption around 1500 cm^{-1}, which corresponds to the IR-active vibron fundamental, consists of multiple bands.

property as shown in Fig. 2(a). The spectra were measured with an arrangement in which the ab plane of the ε crystal was parallel to the propagation direction of the light. When the ab plane of the sample is perpendicular to the electric
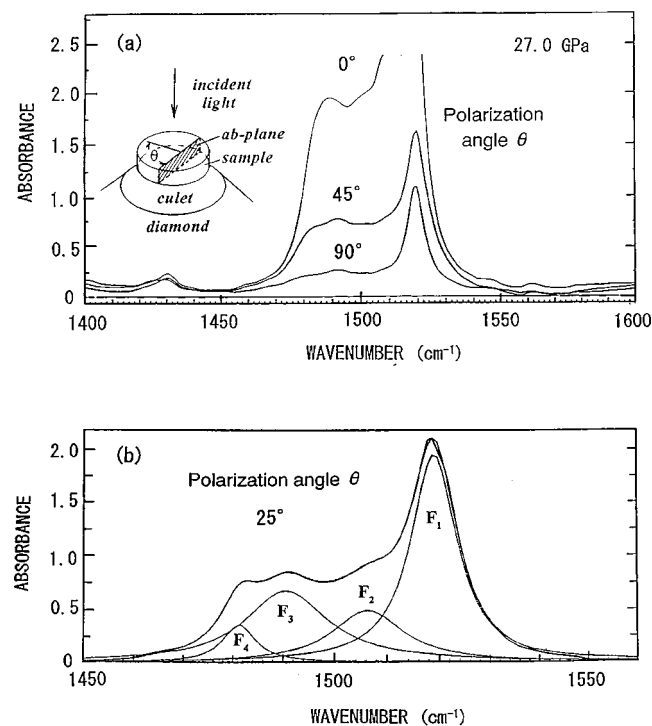

FIG. 2. Absorption spectra of the single crystal sample of the ε phase at 27 GPa. (a) shows the polarization property. The spectra were measured with the ab plane parallel to the propagation direction of the light. When the ab plane is perpendicular to the electric vector of the polarized light, the fundamental absorption seems to be almost a singlet. With a decrease in the angle θ against the polarized light, side bands appeared on the lower-frequency side and these bands grew. (b) illustrates the result of Lorentzian-curve fitting to the spectrum at $\theta = 25°$. The IR vibron fundamental is found to consist of four components labeled F_1, F_2, F_3, and F_4.
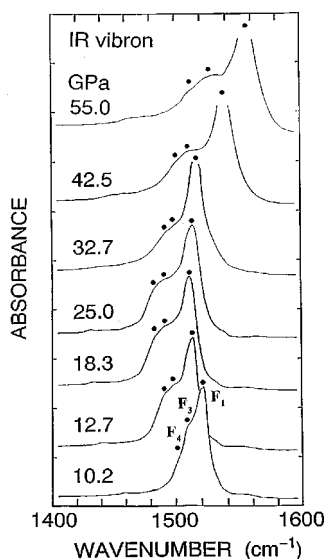
FIG. 3. The pressure change in the IR vibron fundamental for strain-annealed polycrystalline samples. We identified three bands, F_1, F_3, and F_4.

FIG. 4. The pressure dependence of frequency of the IR vibron bands, F_1, F_3, and F_4, together with that of the previously reported Raman vibron (Ref. 5). Open circles and triangles are for the strain-annealed samples; solid circles are for the as-prepared powder sample. Broken lines show the saturating region of absorbance for the as-prepared powder samples. Diamonds correspond to the previous data for the Raman vibron. The lines are a visual guide. The pressure dependence of these IR bands exhibits an inversion at 25 GPa, and the frequencies increase with pressure in the higher-pressure region.

vector of the polarized light, the fundamental absorption seems to be almost singlet considering the accuracy in an arrangement of the crystal direction. With a decrease in the angle θ between the ab plane and the electric vector, side bands were observed at the lower frequency and they grow in intensity. The Lorentzian-curve fitting in Fig. 2(b) suggests that the fundamental consists of four components, that is, the F_1, F_2, F_3, and F_4 bands. In the ab plane, oxygen molecules have been considered to form a layer with a parallel alignment of the molecular axes perpendicular to the ab plane.[8] The present results suggest that there are at least four polarizations in the ab plane for ungerade combinations of the stretching vibrations of the O_2 molecules, that is, the anisotropy of the interaction with adjacent molecules in the layer. The frequencies of the bands are significantly lower by $85-120$ cm^{-1} than the Raman-active vibron ν_R. The difference has already been reported by Swanson $et\ al.$[7] In a previous study using a mixed isotope sample of $^{16}O_2$ and $^{18}O_2$, Agnew, Swanson, and Jones[8] have reported that the IR vibron fundamental was a singlet. The present results claim that it is at least a quartet. Doubling of the Raman band is not observed.

Figure 3 shows the pressure change in the fundamental absorption for the strain-annealed polycrystalline samples. We could identify three bands, F_1, F_3, and F_4, in these spectra. The absorption, with increasing pressure, becomes strong in intensity, and the splitting among the bands becomes larger. The absorption spectra were observed at pressures up to 87 GPa, though the spectrum at 87 GPa showed a sudden increase in background level. Above 92 GPa, the spectra became completely undetectable due to strong absorptions over all frequency ranges from 7900 to 550 cm^{-1}. This sudden behavior is attributed to the insulator-metal transition, namely, a discontinuous band-gap closure. Corresponding to this behavior, the Raman vibron peak merged into the background with a decrease in intensity and also became undetectable.

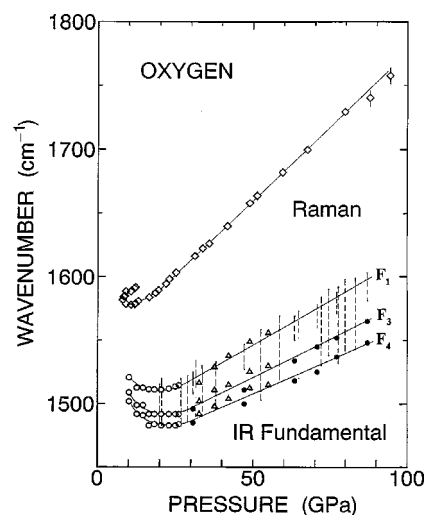The pressure dependence of the frequency for these bands

is illustrated in Fig. 4 together with the data for the previously obtained Raman vibron.[5] The broken lines present a saturating region of absorption for the powder or polycrystalline samples. The frequencies of these bands, with increasing pressure, initially decrease. However, the negative dependence converts to positive with a minimum around 25 GPa. The frequencies between 30 and 87 GPa show a linear increase. The estimated pressure coefficients for F_1, F_3, and F_4 above 30 GPa are 1.7 ± 0.2, 1.2 ± 0.1, and 1.1 ± 0.1 cm^{-1}/GPa, respectively.

Figure 5 shows the pressure dependence of the frequency for the six combination bands with C_1 to C_6 around 3000 cm^{-1} as shown in Fig. 1. The frequencies of four bands, C_1, C_3, C_5, and C_6, were observed as a function of pressure from 10 to 87 GPa, while the C_2 and C_4 bands became indistinguishable at pressures higher than 20 and 58 GPa, respectively. The pressure dependence of C_1, C_2, and C_3 is different from that of C_4, C_5, and C_6. Namely, the former has a minimum at pressures lower than the latter. The C_1, C_2, and C_3 bands can be assigned to the combinations between the Raman and IR vibron fundamentals. The broken lines represent the sum of the frequencies of the F_1 and Raman vibron, $\nu_{\mathrm{IR}\text{-}F1}+\nu_R$ and of the F_4 and Raman vibron, $\nu_{\mathrm{IR}\text{-}F4}+\nu_R$. Considering the anharmonicity of 25 cm^{-1} at lower pressures and 37 cm^{-1} at higher pressures (the value of free oxygen for the gas phase is 24 cm^{-1}), the pressure dependence of the C_1 and C_3 bands is in good agreement with the broken lines. Furthermore, the weak intensity band C_4 may be explained by the overtone of the F_1 band. However, the C_5 and C_6 bands were not explained as overtones or combinations among the four IR vibron fundamentals. Because the pressure dependence is similar to that of the IR vibron fundamentals shown in Fig. 5, they may be due to a
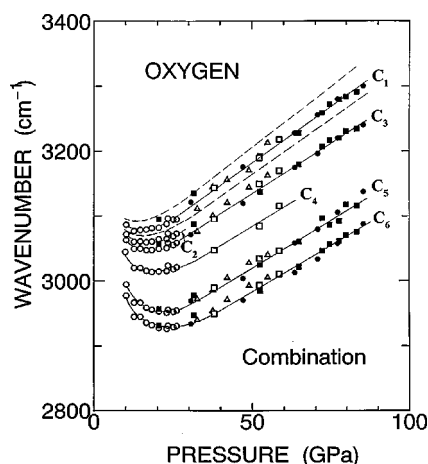
FIG. 5. The pressure dependence of frequency of the combination bands, from C_1 to C_6, to 87 GPa. Open circles and triangles are for the strain-annealed polycrystalline samples; open squares and solid circles and squares are for the as-prepared powder samples. The C_2 and C_4 bands became indistinguishable above 20 and 58 GPa, respectively. The solid lines are a visual guide, and the two broken lines represent the calculated values, $\nu_{IR-F1} + \nu_R$, and $\nu_{IR-F4} + \nu_R$.

combination of zone boundary motions of the IR vibron fundamentals as discussed by Agnew, Swanson, and Jones.[8]

Above 50 GPa, an absorption was observed around 600 cm^{-1}. The pressure dependence is shown in Fig. 6 compared with that of the previously reported Raman-active librons.[5] The agreement with the dependence of Raman libron ν_{L2} suggests that this absorption band is an IR-active vibron bands.

IV. DISCUSSION

The strong absorption of the IR-active vibrons evidently indicates the presence of strong attractive O_2-O_2 intermo-
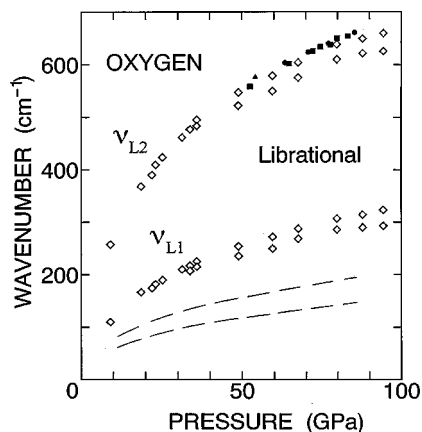

FIG. 6. The pressure dependence of the frequency of the IR libron together with those of the Raman librons reported previously (Ref. 5). Solid circles and squares and the solid triangles are for the IR libron, the frequency of which was in the present detectable region from 550 to 5000 cm^{-1} above 50 GPa. To our knowledge, this band was first observed in the present study. The diamonds represent Raman librons, ν_{L1} and ν_{L2}. The broken lines show the estimated values of $\nu_R - \nu_{IR-F1}$ and $\nu_R - \nu_{IR-F4}$.

lecular interactions. Normally, the frequency difference between the IR and Raman vibrons provides an estimate of the intermolecular interactions. The value of the estimated pressure coefficient of the IR vibron bands above 30 GPa are smaller than the 2.33 cm^{-1}/GPa of the Raman vibron. As a result, the energy difference became larger with pressure (see Fig. 6). The increase in the frequency difference with pressure is evidence for the strengthening of the O_2-O_2 bonds. An interesting thing is that this pressure dependence was similar to that of the reported Raman librons. Such intermolecular interactions can be attributed only to the effect of charge-transfer excitations with the ionic character (O_2^+-O_2^+) as previously proposed[7,10] After the initial decrease in the IR- and Raman-active vibron frequencies at lower pressure, both frequencies increase with increasing pressure. To our knowledge, this turnover in the pressure dependence of the IR vibron is first observed in this study. Agnew, Swanson, and Jones have suggested the weakening of the O-O bond from the behavior of the Raman and IR vibrons in the lower-pressure region than 20 GPa.[8] The positive dependence of the Raman and IR vibrons claims that the O-O intramolecular bond becomes rather stronger above 30 GPa.

According to the optical study by Desgreniers, Vohra, and Ruoff,[1] the absorption edge of the polcrystalline oxygen samples decreases to 0.9 ± 0.1 eV at 82 ± 2 GPa and the near-infrared reflectivity increases at pressures above 90 ± 10 GPa. Extrapolation from the pressure dependence of the absorption edge indicated a band-gap closure at 110 ± 10 GPa. They have concluded that metallization takes place in solid oxygen around 95 GPa. However, it is still unknown whether the pressure-induced metallization is due to continuous overlapping between the bottom of the conduction band and the top of the valence band with pressure similar to iodine.[11] The present results suggest a discontinuous band-gap closure between 87 and 92 GPa. This suggestion does not contradict the previous results by Desgreniers, Vohra, and Ruoff. The structural transition from the ε to ζ phase has been observed between 88 and 96 GPa, and the onset pressures agree. Therefore, the metallization is due to a first-order transition accompanied by the structural transition.

The structure of the ε phase has been proposed to be a monoclinic lattice $C2/m$ containing eight O_2 molecules in a unit cell.[6] The centric lattice has four molecules in the primitive cell. The site symmetries are $C_1(4)$, $C_s(2)$, $2C_2(2)$, $2C_i(2)$, and $4C_{2h}(1)$. The correlation method gives three site symmetries for molecules with an IR-active vibron, that is, C_1, C_s, and C_2. The C_1, C_s, and C_2 molecular sites allow two Raman-active and two IR-active vibrons, one Raman and one IR, and one Raman and one IR, respectively. The present spectroscopic study suggests that the ε phase has four IR-active vibrons and one Raman vibron and that these show mutual exclusion. The results require at least five molecules in the primitive cell. However, the maximum number of the IR vibrons for the proposed space group is only two, and four IR vibrons cannot be explained even if four O_2 molecules center on any symmetry site. The monoclinic lattice should have a lower symmetry than $C2/m$, namely, it is not base centered but primitive. A slight displacement of the molecule centered away from the base center allows this.

Further study on the structural refinement of the ε phase is needed to explain the present results.

V. CONCLUSIONS

In the present study, the vibrational infrared absorption spectra of solid oxygen have been obtained at pressures up to 87 GPa at room temperature. In the ε phase, four IR-active vibron bands, six combination bands, and one libron band were observed, and these frequencies were obtained as a function of pressure. Based on these spectroscopic data together with the previous Raman data, the high-pressure behavior of the intermolecular and intramolecular bonds of O_2 was examined. As a result, strengthening of both the O-O intramolecular bond and the O_2-O_2 intermolecular bond with pressure was suggested. This suggestion was indicative of the stability of the molecular state in the ζ phase. The behavior of the absorption spectra around the metallization pressure suggested a discontinuous band-gap closure between 87 and 92 GPa accompanied by the ε-ζ structural phase transition. The presence of four IR-active vibrons required a lower symmetry for the monoclinic structure of the ε phase than the proposed space group, $C2/m$.

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