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Low-temperature phases of solid oxygen at pressures up to 8 GPa determined by Raman and infrared spectroscopy

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We report studies of vibron, libron, and combined two-libron excitations of solid oxygen in the pressure range up to 8 GPa using Raman scattering and infrared absorption at low temperatures. We took care to ensure that our samples have been close to thermodynamic equilibrium, as confirmed by additional measurements. On the basis of these results we present a revised phase diagram of thermodynamically stable oxygen. There the α phase exists up to temperatures of the β phase and up to a pressure of about 6 GPa, where a clear first-order transition to the δ phase occurs. Our spectroscopically determined phase diagram is in accordance with the structurally determined one by Gorelli *et al.* [Phys. Rev. B **65**, 172106 (2002)]. Inconsistencies with other reported phase diagrams can be attributed to the fact that those samples were not at equilibrium. Furthermore, we provide an indirect proof, using Raman spectroscopy, of the antiferromagnetic order of δ-O_2. The present Raman and infrared investigations together with spectroscopic, x-ray, and neutron data provide a consistent picture of oxygen in the p-T range investigated here.

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I. INTRODUCTION

Solid oxygen belongs to a group of simple molecular crystals examined frequently. It has an antiferromagnetic structure at low temperatures, becomes a diamagnet with pressure, transforms from transparent to colored at increasing pressure, gets a metallic molecular crystal, and even transforms into a superconducting state at ultrahigh pressure.[1] The first pressure-dependent examinations of the oxygen phases were carried out during the 1950s.[2,3] The 1980s saw a variety of spectroscopic and structural studies on the O_2 phase diagram. Nicol *et al.*,[4] using Raman spectroscopy, found a sequence of three solid phases along the isotherm at room temperature. The phase transitions were determined at 5.9, 9.6, and 9.9 GPa. The low-pressure phase was identified by x-ray diffraction studies[5] as β-O_2 a short time later. The phase line between the second and new third phase, the so-called ε phase, was measured down to 100 K. It was presumed that the second phase was α-O_2. Schiferl *et al.*[6] determined the structure of this "orange" phase to be orthorhombic *Fmmm* by means of single-crystal x-ray diffraction. (This phase was named α' temporally,[7–9] but we will use the name δ in the following, as is common today.) The boundaries of the γ phase in the p-T diagram were determined spectroscopically by Yen and Nicol.[10] The p-T ranges of the β and the low-pressure part of the ε phases were characterized by Raman measurements of Hochheimer, Jodl, and co-workers.[8,9] These undoubted phase boundaries are shown by thick solid lines in Fig. 1. Although there exists a large literature on the oxygen phases between the zero-pressure α phase and the high-pressure β and ε phases, this literature is full of contradictions.

Several phase transitions in the regime $p < 3$ GPa and $T < 30$ K were observed in earlier Raman spectroscopic investigations.[8,9,11–15] All these reported phase boundaries are plotted in Fig. 1. Recently we investigated the low-temperature ($T < 30$ K) low-pressure ($p < 1.25$ GPa) range of the α phase by means of Raman spectroscopy.[16] We could exclude the possibility of all second-order phase transitions in the α phase at pressures lower than 4 GPa.

Apart from a phase transition at $p \sim 3$ GPa, Hochheimer, Jodl, and co-workers[8,9] observed no phase transition up to the ε phase, although they interpreted a coexistence range of δ (α') and ε phases for pressures between 5.5 and 7.8 GPa. Mita *et al.*,[17] using Raman spectroscopy, also reported the coexistence of the α and ε phases in that pressure regime. Because both Raman experiments were performed only on samples which have been compressed at low temperatures [15 K (Refs. 8 and 9) and 1.8 K (Ref. 15)] and since we know[16] that this procedure does not produce thermodynamically stable samples, new Raman measurements on equilibrium crystals will be necessary to determine the (equilibrium) phase diagram of oxygen.

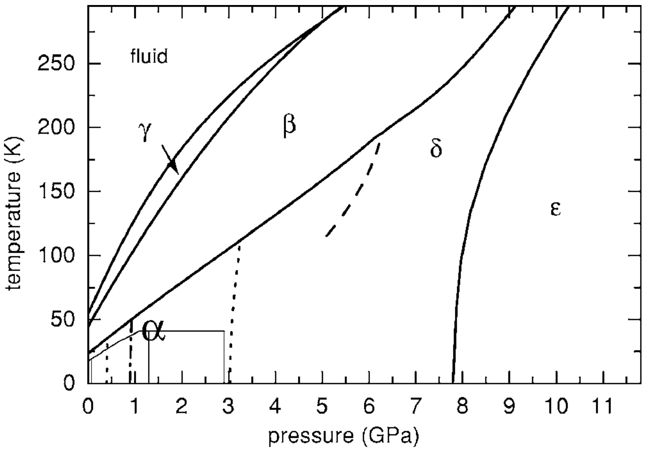

FIG. 1. The phase diagram of oxygen up to 12 GPa and below room temperature determined by Raman spectroscopy. Thick solid lines show the generally accepted phase boundaries. The other phase boundaries are the following: dash-dotted line, Ref. 12; dotted line, Refs. 8 and 9; dashed line, Ref. 13; thin solid line Ref. 15.

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In addition to these discrepancies in optical spectra, structural investigations on solid oxygen also show an inconsistent image. Akahama *et al.*,[18] by increasing pressure at 19 K using monochromatic x-ray-diffraction, observed a direct transformation of the α phase to the ε phase at 7.6 GPa. There was no evidence for the δ phase at temperatures up to 240 K. Later the authors reported that orthorhombic δ structure exists in a very narrow pressure range about 9.4 GPa at the isotherm at 277 K.[19] Contrasting this result, Gorelli *et al.*[20] determined a phase transition $\alpha \rightarrow \delta$ at $\sim$5.5 GPa for several temperatures (50–150 K), also by means of monochromatic x-ray measurements. The main aim of the present precise Raman examinations is to clarify the existence of a δ phase at low temperatures and to resolve the aforementioned contradictions in the literature.

Infrared measurements from Gorelli *et al.*[21]—up to now not confirmed by others—show a narrow peak of the fundamental-mode for pressures between 2 and 8 GPa at low temperatures. We confirmed the unexpected behavior of the spectral feature (at $\sim$1550 cm^{-1}) described by Gorelli *et al.* We further investigated the ir-active vibron, noting its frequency, bandwidth, and band intensity as a function of pressure. A comparison of such results with magnetic properties will allow better insight into the nature and origin of this ir-active mode.

Raman measurements are also interesting with regard to the magnetism of the δ phase. Recently Goncharenko *et al.*[22] determined the magnetic structure directly by neutron diffraction. The authors have found that the intralayer order is antiferromagnetic—as in α-O_2—but the interlayer order is ferromagnetic. The magnetic order of α and δ phases was also indirectly shown by infrared spectroscopy (e.g., Refs. 23 and 24). However, this was not confirmed by Raman spectroscopy. Apart from the question of Raman spectroscopic hints of magnetism in δ oxygen there exist theoretical predictions of Etters *et al.*[25] for the behavior of the Raman frequencies of vibron and libron modes near a possible phase transition from monoclinic to orthorhombic structures of oxygen at zero temperature. New accurate Raman data can prove if the assumptions of Etters *et al.* are correct.

II. EXPERIMENTAL PROCEDURE

Membrane diamond-anvil cells (MDAC's) equipped with type-IIa diamonds (500 μm culet diameter) and inconel gaskets were used to generate high pressures on the samples. The oxygen sample gas (purity 99.998%) was loaded into these high-pressure cells by means of cryogenic loading. The sample dimensions were initially 200 μm in diameter and $\sim$100 μm thickness. A few ruby chips were inserted in the sample to measure the local pressure by the frequency shift of the R_1 ruby fluorescence band. The temperature of each sample was measured by a silicon diode placed very close to one diamond. The resulting uncertainty in the sample temperature is less than ±1 K, as confirmed by several Stokes and anti-Stokes measurements.

The 488-nm or 514.5-nm lines of an Ar$^+$ laser with 200–300 mW on the samples excited Raman spectra that were registered by a triple spectrometer in conjunction with a charge-coupled-device (CCD) camera (Jobin Yvon T64000). Raman vibron spectra were measured in the additive mode. The resolution was around 0.2 cm^{-1}. The frequency accuracy was better than 0.1 cm^{-1} verified by calibration using a source of well-known frequencies in each spectral run. Raman libron and magnon spectra were measured in the subtractive mode with a resolution better than 2 cm^{-1} and frequency accuracy of 0.5 cm^{-1}.

The spectra in the midinfrared spectral region were recorded by a Fourier transform spectrometer (Bruker IFS 120 HR) adapted for high-pressure measurements. It had a beam condensing system similar to the one described in Ref. 26. We used the following experimental setup: a glowbar light source, a KBr beam splitter, and a liquid-nitrogen-cooled mercury cadmium tellurid (MCT) detector. The frequency resolution was chosen as 0.3 cm^{-1}. That means the accuracy in frequency is better than 0.1 cm^{-1}.

To obtain good polycrystalline samples with high optical quality we prefer to vary sample pressure at the highest possible temperatures in β phase. The cooling process has been performed extremely slowly ($\sim$1 K h^{-1}). Spectra were taken during cooling and warming to allow statements about hysteresis effects and the thermodynamic circumstances. The *p*-*T* paths in the phase diagram for the preparation of samples under investigation at lowest temperature were the following: The first sample was produced at the liquid-β phase transition at $\sim$6 GPa and 320 K to avoid the γ-β phase transition breaking the sample by a large increase of volume ($\sim$5%). Then the pressure of the sample was reduced inside the β phase to $\sim$4 GPa at 220 K. Isobaric cooling to 22 K provided conditions to take the first low-temperature Raman spectrum. After warming up to 220 K we increased the pressure on the sample up to 7.75 GPa (δ phase) and cooled down the sample again along an isobar to 22 K. All these changes took place slowly, during days—not minutes or hours. We collected further Raman spectra while very slowly decreasing the sample pressure at low temperature down to again $\sim$4 GPa. Vibron and libron spectra at these conditions are in agreement with spectra collected after isobaric cooling. In support of our method (decompression at low temperature) we produced a new sample from the liquid by the aforementioned procedure and cooled it down isobarically at 6.5 GPa. The resulting Raman spectra at 22 K was in line with the others. Another sample was produced from the liquid (room temperature), and it was cooled down isobarically to about 37 K at 7.1 GPa. We collected infrared spectra while slowly decreasing the sample pressure isothermically down to 2.6 GPa.

Because decompression—in contrast to compression—of oxygen samples at low temperatures does not prevent thermodynamic equilibrium (monitored by Raman and infrared spectra), we applied this method for further Raman and infrared experiments. Our method of sample handling allows us to draw, from our spectroscopic results, conclusions about crystal structure and other sample properties at almost thermodynamic-equilibrium conditions.

III. SPECTROSCOPIC RESULTS AND DISCUSSION

A. Existence of phases and *p*-*T* ranges

The mid-ir spectra at $\sim$37 K are plotted in Fig. 2 as a function of pressure. Two spectroscopic features are observ-

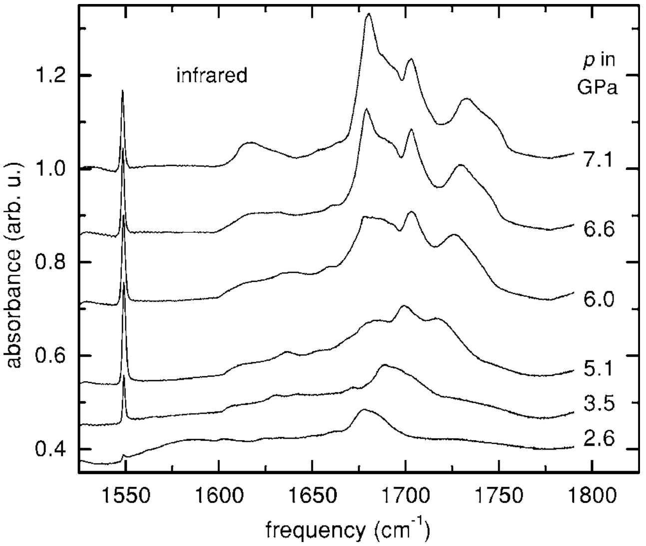

FIG. 2. Midinfrared spectra of the fundamental mode region as a function of pressure at about 37 K. A narrow peak—with almost constant frequency at $\sim$1550 cm^{-1}—is visible besides the broad sideband between 1670 and 1750 cm^{-1}. All spectra were collected while the pressure was released from 7.1 GPa.

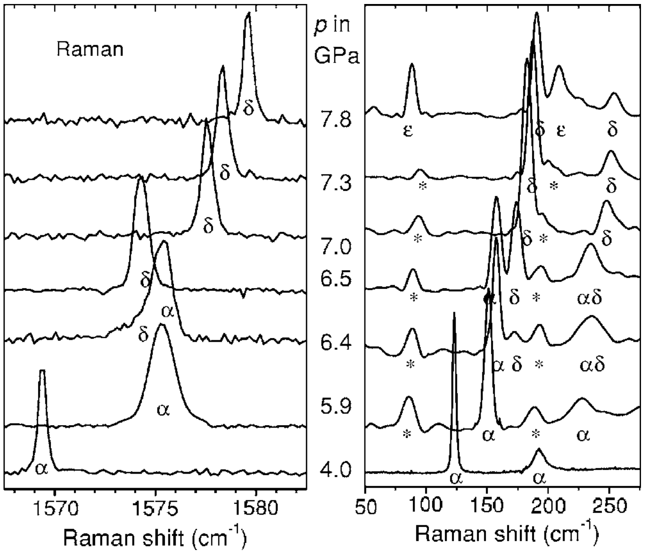

FIG. 3. Raman spectra of vibron (left) and librons (right) as a function of pressure at about 22 K. Peaks belonging to α, δ, or ε phases are, respectively, identified. Peaks in the libron spectra which are marked with asterisks originate from residuals of the ε phase (see text). The spectra at 4.0, 6.5, and 7.8 GPa were collected after isobaric cooling of the sample, the other spectra while the pressure was released.

able in this spectral range. The first one is the broad phonon sideband between 1670 and 1750 cm^{-1}, which is well known at ambient pressure (e.g., in Ref. 27). Gorelli *et al.*[21,28] described this sideband also at higher pressure. The ir-active sideband shows a more pronounced structure (exceptionally at $\sim$1680 cm^{-1}) for pressures greater than $\sim$6 GPa than for pressures lower than $\sim$6 GPa. This might be a consequence of the α-δ phase transition. The second spectral feature in the mid-ir spectra is the narrow peak with almost constant frequency at $\sim$1550 cm^{-1}. The existence and disappearance of this mode at $p \lesssim 2.5$ GPa was described by Gorelli *et al.*[21] Our experimental results are in agreement with their data and prove the existence of this ir-active peak. Its frequency shows almost no pressure dependence. The intensity of this very narrow peak rises with increasing pressure, but no distinct discontinuity is detectable.

In contrast to the ir spectra with no obvious hints for phase transitions, the Raman spectra show clear indications of different phases and phase transitions. The pressure evolution of the Raman vibron and libron modes at low temperature is shown in Fig. 3. In the spectra up to 6.5 GPa the vibron and two libron modes from the α phase are visible. At 5.9 GPa the α phase vibron is very broad, and two additional broad peaks are visible in the lattice mode range. These modes can be explained by an admixture of the crystal structure by parts with an ε-like structure. Those are present in all spectra up to pressures of the ε phase—even in the spectrum at 6.5 GPa on sample 2 which has never been in the ε phase. (That indicates that our samples were not in perfect thermodynamic equilibrium.) Near 6.5 GPa the δ-phase vibron appears at lower frequency and two additional librons at higher frequencies appear. From 7 GPa only features that can be assigned to δ-O_2 remain. Two strong narrow peaks in the libron spectrum at 7.78 GPa indicate coexistence of δ and ε oxygen. In the related vibron spectrum no indications for the ε phase exist because this spectrum was collected at a bit lower pressure: 7.73 GPa.

Figure 4 shows the frequencies and bandwidths of all Raman modes (vibron and librons) as functions of pressure between 4 and 8 GPa. By means of the frequency evolution a phase transition from α to δ structure at $\sim$6.5 GPa is visible. The vibron frequency increases with increasing pressure inside the α phase ($\sim$2.6 cm^{-1}/GPa), jumps 1.3 cm^{-1} to lower energies at the phase transition, and increases again—but more rapidly—in the δ phase ($\sim$4.3 cm^{-1}/GPa). The frequencies of the α phase librons (B_g and A_g; cf. Ref. 29) increase with increasing pressure ($\sim$13 cm^{-1}/GPa). At the phase transition the libron frequencies jump $\sim$16 cm^{-1} to higher energies. The least-energetic libron shows the same slope of pressure-dependent frequency in δ as in α oxygen. The frequency of the higher-energetic libron increases less rapidly with pressure ($\sim$4.5 cm^{-1}/GPa) in the δ phase. The principle features of the libron spectra of α and δ phases are two librons. The less-energetic is more intense. Both remain in the ε phase, but the frequency jumps at the δ-ε phase transition are larger ($\sim$50 and $\sim$100 cm^{-1}) than those at the α-δ phase transition and differ in sign. The volume increase at the α-δ phase transition is $<0.5\%$,[20] whereas it is $\sim$3% at the δ-ε phase transition.[19] Of more importance is the difference in magnetism at both phase transitions: while the magnetic exchange interaction shows a jump by $\sim$3% at the α-δ phase transition[22] the δ-ε phase transition is caused by the magnetic collapse[30] that is responsible for the size and sign of the jumps in our Raman frequencies. It is evident that the pressure dependence of the Raman vibron and libron frequencies indicates two phase transitions, and it shows that these phase transitions are of first order.

The bandwidths of the Raman modes show, mainly, the ordinary pressure behavior: they increase with increasing

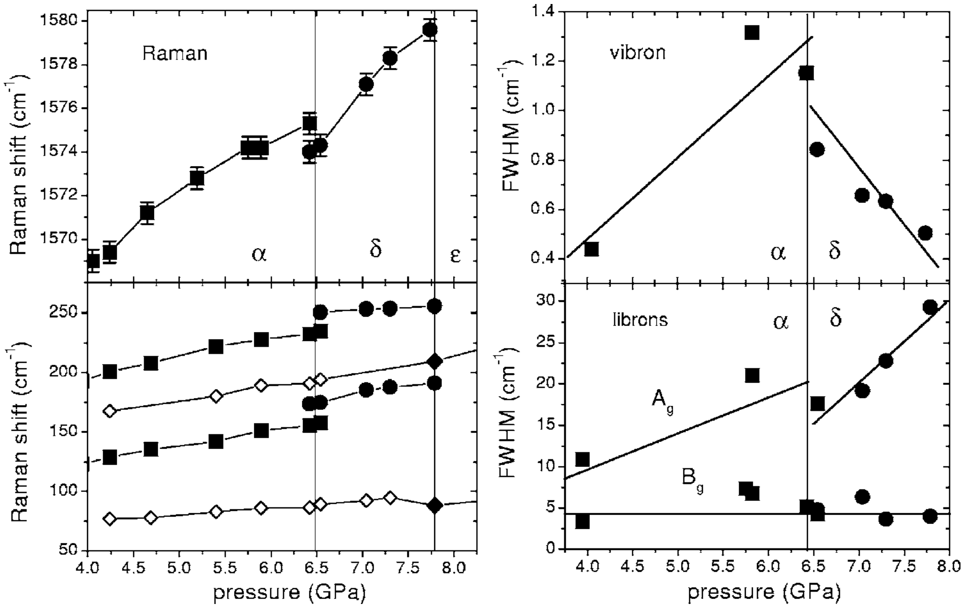

FIG. 4. Frequencies (left) and bandwidths (right) of Raman vibron (upper) and libron (lower) modes as a function of pressure at ~22 K. The quality of the spectra at 4.7 and 5.4 GPa allowed evaluation of the frequencies but not the widths of the bands. The phase transitions α-δ and δ-ε (latter one only in the libron spectra) are visible by clear jumps in frequencies. Open symbols represent contributions of ε phase-like contributions in spectra of lower pressure phases. (The solid lines in the bandwidth diagrams are aids to the eye to show tendencies.)

pressure. The bandwidth of the A_g libron increases by ~2 cm^{-1}/GPa inside the α phase, the B_g libron shows less distinctive pressure behavior, and the related libron in the δ phase maintains a constant bandwidth. The continuation of the A_g libron in the δ phase shows a steeper pressure evolution of its bandwidth. The bandwidth of the vibron as a function of pressure is more noticeable than that of the librons. Inside the α phase the bandwidth increases—what we describe as an influence of the perturbation by ε phase-like parts in the α phase crystal as a consequence of nonhydrostatic components of the stress in the sample. On the contrary the decrease of vibron bandwidth in δ phase is unusual. We explain this behavior as an indication that the higher the pressure is the more ordered the crystal becomes—or with higher pressure the collective vibrational excitations in the crystal have less effect in the ε admixture. One can recognize phase transitions from bandwidth evolution as a function of pressure.

As one main result of our Raman investigation we have established a revised p-T phase diagram of solid oxygen at thermodynamic equilibrium (shown in Fig. 5). This is in accordance with the structural analysis of Gorelli *et al.*[20] In contrast to structural investigation of Akahama *et al.*,[18] the δ phase exists at low temperatures in the work of Gorelli *et al.*—as well as in our Raman experiment.

B. Thermodynamic of low-temperature oxygen phases

The result that the δ phase exists at low temperatures in the structural study presented by Gorelli *et al.*[20] and in our Raman investigations emphasizes the importance of thermodynamic stability of these samples. Akahama *et al.*[18] produced their samples at low pressure, cooled them down to the required temperature, and applied pressure along isotherms at 1.8 K. Therefore they overpressed the α phase at low temperature. The unspectacular phase transition α-δ $(\Delta V/V < 0.5\%)$ did not occur. Only the phase transition to the ε phase—connected with more drastic changes in the sample ($\Delta V/V \sim 3\%$; magnetic collapse)—was observed. As did Gorelli *et al.*, we have measured no sharp phase line (shaded area in Fig. 5) between the α and δ phases. The uncertainty in the phase transition is connected with uncertainties in pressure, temperature, and sample history (time) on the one hand and with the kinetics of the phase transition on the other hand.

Two questions remain. First, is the measured width of the phase transition with changing pressure caused by the transition or is it only a thermodynamic effect? Second, why do we see relics of ε-like structure in the α and δ phases whereas we believe the samples are nearly those of equilibrium. We will try to answer these two questions in the following.

Since in Raman spectroscopic investigations the laser is always a possible influence of thermodynamic equilibrium conditions, we will look to the infrared spectrum of the mid-ir peak for the answer to the first question. Figure 6 shows the frequency (upper) and the bandwidth (lower) data of the infrared-active vibron as a function of pressure at low

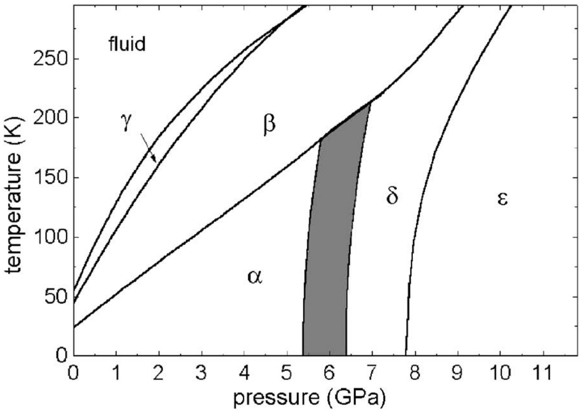

FIG. 5. Phase diagram ($p < 12$ GPa and $T < 300$ K) of solid oxygen at equilibrium conditions as a result of the actual Raman measurements.

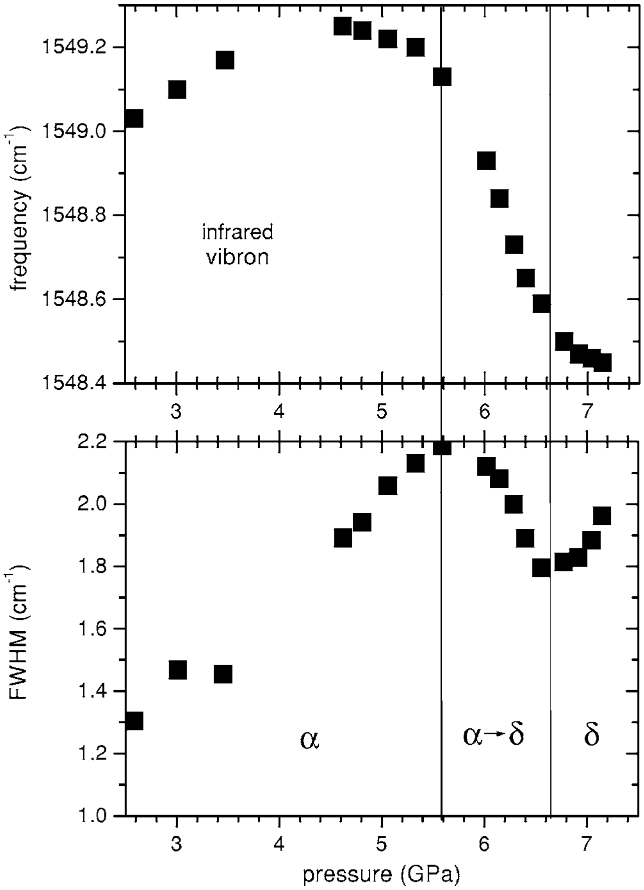

FIG. 6. Frequency and bandwidth of the infrared-active vibron as a function of pressure at ~37 K. The range of the phase transition α-δ is about 1 GPa.

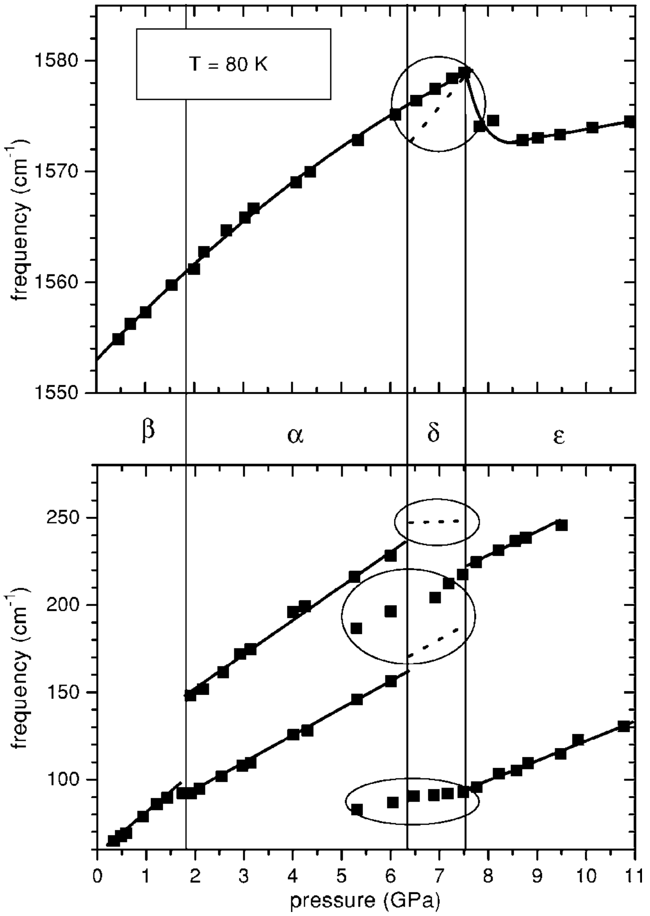

FIG. 7. Frequencies of vibron and librons (symbols) as functions of pressure from the Raman experiments of Hochheimer, Jodl, and co-workers (Refs. 8 and 9) at 80 K. (Solid lines are guides to the eye.) Actual results are shown by dotted lines. Phase boundaries and the nomenclature of phases are given with the actual knowledge. Encircled areas point up the differences between the explanation given in Refs. 8 and 9 and the actual explanation (cf. Fig. 4).

temperature. These spectroscopic features display a phase transition range that is about 1 GPa in width. The vibron frequency increases inside the α phase (~0.07 $\mathrm{cm}^{-1}/\mathrm{GPa}$), decreases by ~0.6 $\mathrm{cm}^{-1}/\mathrm{GPa}$ in the phase transition range and is more or less constant in the δ phase. The bandwidth increases also in α oxygen with increasing pressure (~0.3 $\mathrm{cm}^{-1}/\mathrm{GPa}$), falls by ~0.4 $\mathrm{cm}^{-1}/\mathrm{GPa}$ in the phase transition range, and increases again in δ oxygen. Since both curves have their steepest variation in the phase transition region, these spectroscopic features offer an answer to our first question. The time between taking spectra for two data points in the diagram was typically some hours. At some pressure we collected a spectrum, waited for days while maintaining the same conditions, and measured again. We detected no change in the spectrum. Therefore we exclude the possible influence of thermodynamics on the width of the phase transition.

To answer the second question one has to recognize that relics of ε-like structure are present in all Raman spectra in high-pressure α and δ phases, especially in the libron spectrum at 6.5 GPa on sample 2 that has never been in the ε phase. Since the contributions of these ε peaks to libron spectra vary for different measurements, we presume that the closer we come to equilibrium conditions in our samples, the smaller are ε-like librons in the libron spectra of the α and δ phases. The results of earlier Raman measurements can now be explained by this assumption. Mita *et al.*[17] have observed at 1.8 K only α and ε phases and, in a wide range of pressures, between 5 and 9 GPa, a mixture of both phases. Because the authors pressed their sample at 1.8 K they produced much stress in the sample. Therefore their samples were far from equilibrium and the portion of ε-like structure in the α phase was high. Because of this, thermodynamic disequilibrium no δ structure was built up in the sample. At higher pressures a transition from the mixture to pure ε phase occurred.

The Raman results reported by Hochheimer, Jodl, and co-workers[8,9] can be explained in a similar way. Figure 7 shows their spectroscopic results achieved by isothermal compression at 80 K. The following reinterpretation is made with the actual knowledge of phase transition lines and by comparing old and current Raman results. At around 5 GPa features of both monoclinic structures, α and ε oxygen, are visible in the libron spectrum. The libron modes of α-O_2 disappear at about 6.5 GPa, which is the pressure of the phase transition to the δ phase in thermodynamic equilibrium. Contrasting this result, the vibron behaves differently.

Its frequency increases with increasing pressure, indicating a continuation of the α phase. The transition to the ε phase begins at about 7.5 GPa, or ~0.3 GPa lower in pressure than the phase transition at equilibrium. These discrepancies between spectroscopic results of the thermodynamically unstable sample in the internal range and those in the external range can be explained with assistance of the model[31] of O_4 complexes in the ε phase. The distances between centers of masses of the molecules change as a consequence of stress and inhomogeneities in the sample (cf. Fig. 131 of Ref. 1). Therefore the collinear molecules move pairwise together—without formation of O_4 complexes. This change in the intermolecular distance [prestage of an O_4 complex—either $(O_2)_2$ or $O_2^+O_2^-$] influences the librational motion of the molecules whereas the internal vibration is not (or is less) influenced. At higher pressures than 7.5 GPa a collective formation of O_4 complexes starts, and with this the energy of vibration changes.

In summary, our work shows that it is important to investigate samples in (or near) thermodynamic equilibrium conditions. In systems like oxygen such conditions are only reachable by a very careful handling of the sample (sample preparation, p-T paths). Many reported results in the literature give an account of the related (disequilibrium) sample but not of oxygen in general. In contrast, the phase diagram that we present in Fig. 5 shows the phase diagram of solid oxygen at thermodynamic equilibrium.

C. Magnetism in the α and δ phases

The most prominent feature of the magnetism in the α phase of solid oxygen visible in the Raman spectrum is the magnon mode at ~27.2 cm^{-1}. One might expect that by applying pressure—i.e., reducing distance between neighboring magnetic molecules—one would produce an increase of the magnetic coupling. This does not occur: the intensity of the magnon mode diminishes with increasing pressure.[15,16] At pressures higher than 3 GPa—where the ir-active vibron mode at ~1550 cm^{-1} exists—it is so weak that it is not possible to detect it with our conventional Raman system. Therefore one cannot use the magnon mode to study magnetism in α and δ oxygen at higher pressure by Raman spectroscopy. We have identified an additional phenomenon of α-O_2 that is intimately connected with its magnetism: Two-libron excitations have been observed in our zero-pressure Raman measurements.[32] These we explained as originating with magnetic coupling of two molecules in the primitive cell performing librations. In our recent low-pressure Raman study[16] on α oxygen we found that due to an enhancement of the spin coupling mechanism, the intensities of two-libron excitations increase by a factor of about 5 as one applies pressure from 0 to 1.25 GPa. Therefore, the pressure dependence of frequencies and intensities of these two-libron excitations have to be investigated in the pressure range up to 8 GPa to obtain Raman spectroscopic information about magnetism of the high-pressure α phase and the δ phase at low temperatures.

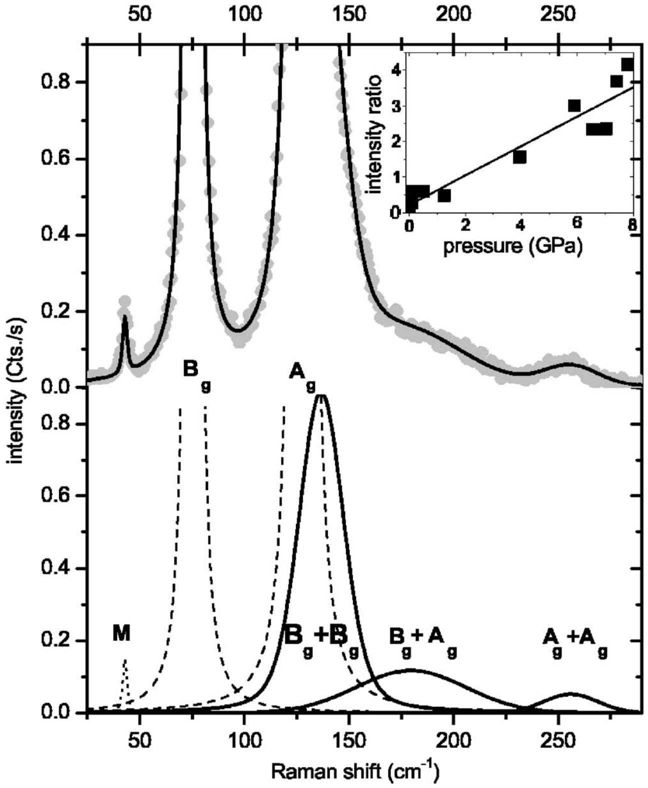

FIG. 8. The oxygen Raman spectrum in the low-energy range at $p=1.25$ GPa and $T=16$ K. The measured spectrum is shown by light gray symbols and its fit by a thick solid curve in the upper part. Single contributions to this fit are shown by different lines in the lower part: libron modes (dashed line), magnon mode (dotted line), and two-libron excitations (thin solid line). The inset shows the intensity of the two-libron excitations relative to that of the one-libron modes as a function of pressure in α and δ phases.

Figure 8 shows the low-energy Raman spectrum of α oxygen at 1.25 GPa. At this pressure one can see both magnetically caused features: the higher-energy magnon and three two-libron modes. Whereas the magnon mode vanishes with increasing pressure, the two-libron excitations are seen throughout the α phase and become more intense at higher pressures. This trend—already observed at low pressure[16]—continues even in the δ phase, where also the two-libron excitations exist. The intensity of the two-libron excitations relative to the intensity of the one-libron excitations is shown in the inset in Fig. 8. We scaled the intensity to the value at 2 GPa. The ratios $I(p)/I(2\text{ GPa})$—from experimental data—are shown for different pressures in Table I. Next we would like to model theoretical this behavior $I(p)$. The intensity ratio $I(p)$ is proportional to the magnetic exchange interaction $J(p)$. We used the lattice parameters re-

TABLE I. Intensity ratio of two-libron excitations (I) and magnetic exchange interaction (J) for α oxygen at low temperature and different pressures. Both measurements are scaled to the value at $p=2$ GPa.

Pressure p (GPa)	2	4	6	7.8
$I(p)/I(2\text{ GPa})$	1	1.6	2.8	3.4
$J(p)/J(2\text{ GPa})$	1	1.7	2.6	3.3

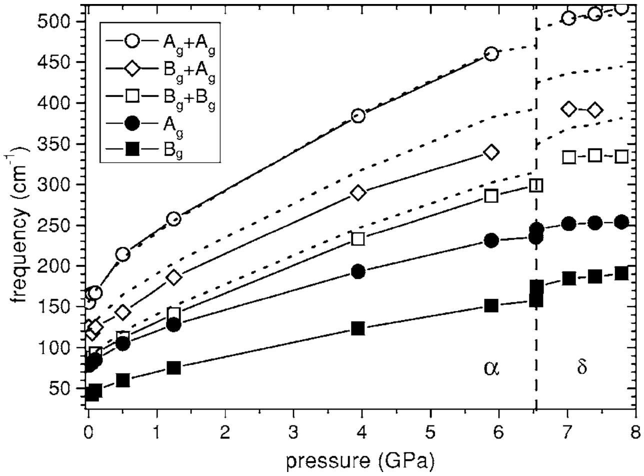

FIG. 9. Frequencies of the Raman-active one-libron and two-libron excitations in α and δ oxygen as a function of pressure (0–8 GPa) at $T \approx 20$ K. Measured data are plotted with symbols. Dotted lines represent frequencies, which result from simple addition of frequencies from librational ground states.

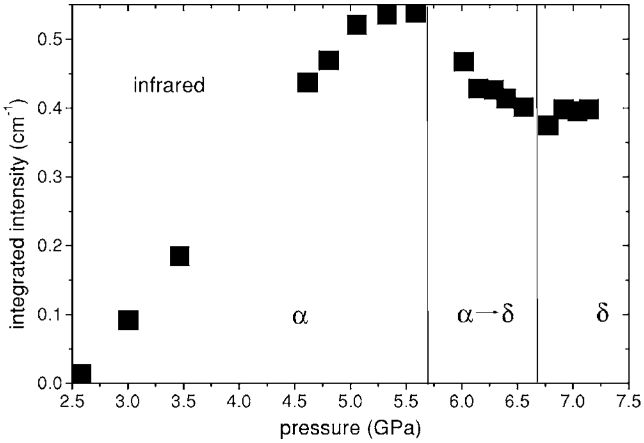

FIG. 10. Integrated intensity of the ir-active mode at $\sim$1550 cm^{-1} as a function of pressure. Phase ranges are marked as described in Sec. III B.

ported by Akahama *et al.*[18] to calculate the distance $R(p)$ between neighboring molecules as a function of pressure p. From these we evaluated the magnetic exchange interaction using the formula

$$J(p) = J_0 \exp[-\alpha R(p) + \alpha R_0], \tag{1}$$

where $J_0 = 19.6$ cm^{-1}, $\alpha = 3.765$ Å^{-1}, and $R_0 = 3.187$ Å.[33] Table I shows theoretical values of $J(p)$ relative to normalization at 2 GPa. The excellent agreement between experiment $[I(p)]$ and theory $[J(p)]$ confirms a previous[16] assumption that one can explain the two-libron intensity and its increase by applying pressure—i.e., reducing intermolecular distances to strengthen the magnetic coupling.

Our results show that the progression of the two-libron intensity is continuous at the α-δ phase transition, whereas the frequencies of the two-libron excitations distinctly jump at the pressure of the phase transition. Figure 9 shows the frequencies of librons (solid symbols) and two-libron excitations (open symbols) as a function of pressure. The simple sums of the ground-state frequencies are shown by dotted lines. As was the case at low pressures[16] the difference between the frequencies of the two-libron excitations and the arithmetic sum of the ground-state frequencies can be attributed to the mechanical anharmonicity of the related libron potential. But the size of this difference remains constant at the α-δ phase transition. We also conclude from the continuous behavior of the frequency difference $2\omega_{libron} - \omega_{two\text{-}libron}$ and the two-libron intensity in the whole pressure range of α and δ oxygen that δ-O$_2$ is antiferromagnetically ordered. This is an indirect proof of the antiferromagnetic order of δ oxygen by Raman spectroscopy. Unfortunately the determination of Raman intensities is not accurate enough ($\Delta I \sim 5\% - 10\%$) to determine a reduction of the magnetic exchange interaction $J(R)$ at the phase transition α-δ as one would expect according to the direct measurements of the magnetic order inside δ-O$_2$ reported by Goncharenko *et al.*[22] ($\Delta J \sim 3\%$).

To evaluate the possibility of a magnetic origin of the ir-active mode at $\sim$1550 cm^{-1} we will recapitulate the experimental results: Both the disappearance of the Raman magnon mode and the appearance of the ir vibron mode happen at $\sim$2.5 GPa. Gorelli *et al.*[21] explained the presence of this ir-active vibron as due to the long-range antiferromagnetic order of the molecular spins producing a doubling of the primitive cell. In our opinion there are three arguments against this model. First, since the α phase possesses also one molecule per primitive structural unit cell and two molecules in the magnetic cell because of the antiferromagnetic spin arrangement, one would expect an ir-active mode at zero pressure. In our recent highly sensitive infrared measurements[27] we could not detect such an ir-active mode. Second, the magnon vanishes continuously (cf. Refs. 15 and 16). And third, Goncharenko *et al.*[22] in their neutron-diffraction study saw no distinct change of the magnetic structure inside the α phase. Accordingly, we argue that the appearance of the vibron and the disappearance of the magnon mode are independent and both occur only accidentally at $\sim$2.5 GPa.

The aforementioned model of a precursor of an O$_4$ complex in the pressure range 2.5–7.8 GPa (cf. Sec. III B) could also explain the existence of this weak ir-active vibron mode at 1550 cm^{-1}. Due to minor modifications in geometry—molecules approach pairwise—selection rules change and the ir-active vibron mode is then allowed, even though it is forbidden for the structure of the pure α phase. The intensity of this ir mode behaves like a magnetic exchange interaction provided that it is allowed. In Fig. 10 its integrated intensity is plotted as a function of pressure. The peak intensity at $\sim$2.5 GPa increases strongly with increasing pressure inside the α phase, decreases in the broad range of phase transition, and is constant inside the δ phase. The intensity behavior in the vicinity of the phase transition α-δ can be explained by the reduction of magnetic exchange interaction as a result of the rearrangement of the interlayers.[22]

D. α-δ phase transition: Comparison between theory and experiment

In this section we compare theoretical predictions of structure and dynamics with experimental results. The structure of the monoclinic α phase ($C2/m$) is similar to that of the orthorhombic δ phase ($Fmmm$). Therefore one would expect a second-order phase transition between both phases at a first glance. In addition to our current Raman data (cf. Figs. 3 and 4) there is structural data from monochromatic x-ray diffraction experiment of Gorelli *et al.*[20] These show clearly the first-order character of the phase transition $\alpha \rightarrow \delta$. Those authors have shown in their Fig. 2 the ratio b/a of the lattice parameters and the monoclinic angle β' as functions of pressure near the phase transition for different temperatures. Both features (b/a and β') distinctly change at the pressure of the phase transition (~5.5 GPa). Remarkably, the sign and size of the change of β' coincide with theoretical values determined by lattice-dynamic calculation of Etters, Kobashi, and Belak[25]—only the transition pressure deviates. This was calculated to be 2.4 GPa by Etters *et al.* Since the authors calculated this transition pressure to be 0.6 GPa in their preceding article,[34,35] they evaluated the sensitivity of this transition to the details of the potential. The size of the jump of the b/a values at the phase transition also shows discrepancies between theory and experiment by a factor of about 5.

Etters *et al.* published the frequency shifts of vibron and libron modes as a function of pressure. To best compare experiment and theory, the frequency of the vibron modes are plotted together in Fig. 11. The frequency examined in the actual Raman investigation is shown by solid quadrates for the α phase and by solid circles for the δ phase. The scaled vibron frequency data calculated by Etters *et al.* are plotted as a thick solid line. [We had to multiply the computed pressure (2.4 GPa) by a factor of 2.7 to make the calculated transition pressure consistent with the measured one (6.5 GPa). Additionally, the frequency shift $\delta\omega$ was scaled to make the theoretical and experimental frequency shift inside the α phase near the phase transition ($\omega_{p_{\alpha-\delta}} - \omega_{p=0} = 22.7\ \text{cm}^{-1}$) comparable.] The very good agreement between the Raman data and the scaled theoretical data inside the α phase is remarkable. In the δ phase, by contrast, the experimental frequency values vary more rapidly with pressure than do the calculated ones. The lower part of Fig. 11 shows an expanded portion of the upper diagram near the phase transition. It is obvious that the jump of measured frequencies coincides in direction and size with the theoretical frequency jump. Furthermore, the jumps in frequency of the libron modes at the α-δ phase transition that are observed in the Raman experiment are consistent with those calculated in the lattice dynamic study (see Table II).

To summarize, the comparison between theory and experiment, for x-ray as well as Raman experiments, has shown a very good agreement in the behavior of the features near the phase transition $\alpha \rightarrow \delta$. We confirm the method that Etters *et al.* have used and also their approach for potentials.

IV. CONCLUSION

We have performed Raman scattering and infrared absorption studies on solid oxygen at low temperatures in the pressure range up to 8 GPa. We varied the pressure in the high-temperature β phase but not at low temperature. To save time, we lowered the sample pressure very slowly in one run. These results agreed with those obtained by isobaric cooling. In this procedure one keeps the samples close to thermodynamical equilibrium, thereby maintaining better optical crystal quality than in earlier experiments. We investigated the low-lying fundamental excitations such as vibron, libron, and combined two-libron excitations as a function of pressure and temperature.

Our studies using Raman and infrared spectroscopy show for the first time the existence of the δ phase of oxygen at low temperatures. We show that the influence of sample handling (sample preparation, p-T path) is very important for thermodynamic equilibrium conditions and therefore also for the existence or nonexistence of phase structures. This result

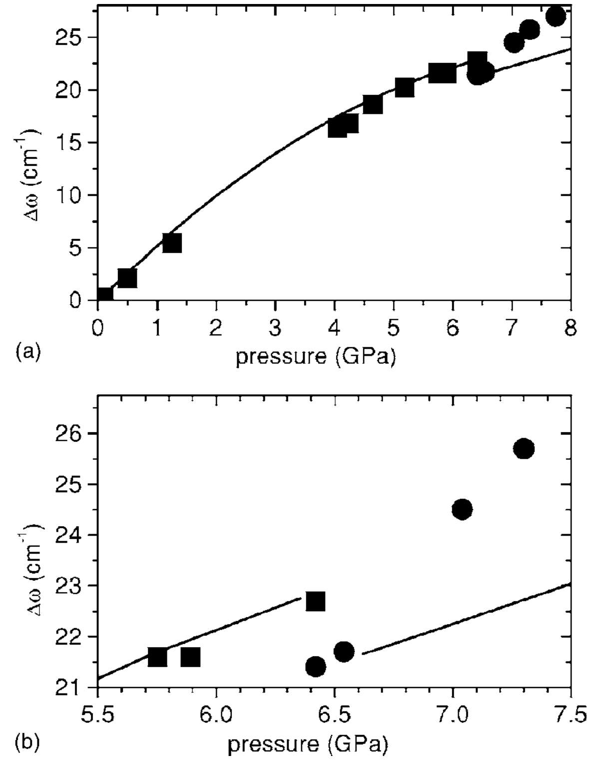

FIG. 11. (a) Shift in the vibron frequency versus pressure. Squares and circles represent actual data obtained by Raman spectroscopy in the α and δ phases, respectively. Thick solid lines represent the results of a calculation in consideration of the magnetic unit cell (Ref. 25). (The theoretical data are scaled with respect to the pressure and frequency shift of the phase transition.) (b) Expanded detail of (a).

TABLE II. Jumps in mode frequencies at the transition from the α phase to the δ phase relative to the increase of frequency $\delta\omega$ with increasing pressure ($\delta\omega = \omega_{p=p_{\alpha-\delta}} - \omega_{p=0}$).

	A_g libron	B_g libron	Vibron
Calculated data at $T=0$ K[a]	+5%	+13%	−6%
Measured data at $T=22$ K	+9%	+14%	−6%

[a] Reference 25.

is of fundamental interest, especially for solid oxygen, where there is contradicting literature (because of nonequilibrium conditions of the samples). It is important also for other substances and sensitive systems, such as F_2 or CS_2. We present in Fig. 5 a revised equilibrium phase diagram of oxygen. This is in accordance with the phase diagram presented by Gorelli *et al.*[20] as a result of structural x-ray investigations. Other published phase diagrams are not equilibrium phase diagrams. On this basis we reinterpreted the old Raman spectra reported by Hochheimer, Jodl, and co-workers[8,9] and provide a coherent interpretation of current knowledge of Raman, infrared, and x-ray data.

The contributions of an ε-like structure to the libron—but not to the vibron—spectra in the α and δ phases in the actual Raman experiments can be explained by the model of a prestage of an O_4 complex. The existence of the midinfrared mode at about 1550 cm^{-1} between 2 and 8 GPa can also be explained with this model.

We confirm the assumption[16] that the intensity of the two-libron excitations is correlated with the magnetic exchange interaction. From the continuous behavior of the two-libron intensity and the difference of measured and calculated two-libron frequency in the whole pressure range of α and δ oxygen we proved indirectly the antiferromagnetic order of δ-O_2 like in α-O_2 by Raman spectroscopy.

In the present Raman and infrared spectroscopic investigations and the discussion presented in this article, spectroscopic, x-ray, and neutron data provide a consistent picture of oxygen in that p-T regime.

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