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2004 J. Phys.: Condens. Matter 16 6415

(http://iopscience.iop.org/0953-8984/16/36/008)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) 6415–6430 PII: S0953-8984(04)80702-1

Raman spectroscopic investigations of the antiferromagnetic α phase of solid oxygen at low pressure (up to 1.25 GPa)

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Received 7 May 2004, in final form 9 August 2004
Published 27 August 2004
Online at stacks.iop.org/JPhysCM/16/6415
doi:10.1088/0953-8984/16/36/008

Abstract

Elementary magnon, libron and vibron excitations as well as combined two-libron excitations of solid α oxygen have been investigated by means of Raman scattering at several isobars in the pressure range up to 1.25 GPa. We deduced the band frequency, bandwidth and relative band intensity of all modes as a function of temperature and pressure. On the basis of these results we can exclude the possibility of all second-order phase transitions in the low temperature, low pressure range of oxygen stated in the literature. The disappearance of the sublattice magnetization σ could be estimated from the frequency of the higher energy magnon mode at the critical pressure $\sim$7.7 GPa which is in the vicinity of the phase transition from the antiferromagnetic ordered δ phase to the non-magnetic ε phase. The change of several spectroscopic features under increasing pressure clearly indicates that anharmonic contributions in the libron potential are altered.

1. Introduction

Solid oxygen combines the properties of a molecular crystal and those of a magnetic material. The low temperature phase α-O_2 is the only electron-spin antiferromagnetic insulator consisting of a single element [1]. Furthermore, it is a two-sublattice antiferromagnet [2, 3] with two molecules in the magnetic cell and only one molecule in the primitive structural cell (monoclinic) with space group $C2/m$ [4]. This low temperature α phase exists up to pressures of 7.6 GPa according to recent x-ray data reported by Akahama *et al* [5], whereas

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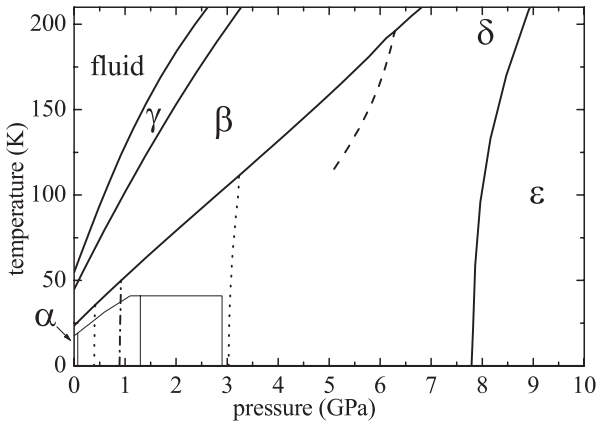

Figure 1. The phase diagram of oxygen up to 200 K and 10 GPa. The generally accepted phase boundaries are shown by thick solid lines. The other eight phase boundaries are: dashed–dotted—[7]; dotted—[8, 9]; dashed—[10]; thin solid—[12].

Gorelli *et al* [6] determined, also recently, a phase transition $\alpha \rightarrow \delta$ at 5.5 GPa by means of x-ray measurements. In contrast, several phase transitions in that p–T regime ($p < 3$ GPa, $T < 30$ K) were observed in earlier Raman spectroscopic investigations: Meier *et al* [7] reported a phase transition at ∼0.9 GPa; Hochheimer and Jodl [8, 9] proposed an intermediate phase $\bar{\alpha}$ between the α and δ phases in the low temperature region between 0.4 and 3.0 GPa; Yen and Nicol [10] suggested a new phase, δ'-O_2, as an intermediate phase between $\bar{\alpha}$ and δ oxygen at $T = 120$ K; Mita *et al* [11, 12] claimed to have found several phase transitions along the 1.8 K isotherm via small discontinuities in the frequencies of libron and magnon excitations at 0.07, 1.3 and 2.9 GPa. All these reported phase boundaries are plotted together in figure 1, in addition to the well known phase lines of the first-order transitions.

Common to all these optical investigations [7–9, 11, 12] is the fact that (1) the authors assigned minor changes in phonon spectra to possible phase transitions and (2)—what is even more relevant—the pressure on the sample was varied at low temperatures. Therefore the samples were not necessarily in thermodynamically stable conditions. Pressure changes at low temperatures without mechanical relaxation may cause reactions in the sample similar to those of (second-order) phase transitions; i.e. applying pressure to a crystal in the cold state will produce local stress and strain and there is almost no possibility for a continuous elastic relaxation at these temperatures on finite timescales. Consequently, at a certain pressure the strain on the sample is too high with respect to the mechanical stability and will cause some mechanical and structural alterations at a single stroke. Resulting changes in spectra at this specific pressure might be interpreted as a hint of a possible phase transition. But a phase transition does not occur at these p–T conditions if one applies pressure quasistatically at higher temperatures and then allows relaxation in the sample and isobaric cooling. Due to this effect and due to small changes in optical spectra, previously reported phase transitions in this p–T range ($p < 3$ GPa, $T < 30$ K) are questionable (figure 1). To avoid this misinterpretation of changes in spectra and to achieve samples in thermodynamical equilibrium with good optical quality, it is essential to change the pressure only at the highest possible temperatures in the β phase and to measure along isobaric paths in the p–T diagram.

Besides Mita *et al* [12] including isothermal runs (at 1.8 K) in their studies, these authors also made measurements under isobaric conditions—during warming—to determine the temperature where the magnon excitation disappeared. This always happened at temperatures

lower than the temperature of the α–β phase transition ($T_{\alpha,\beta}$). Therefore, they claimed an additional magnetic phase transition inside the structurally determined α phase. This result is in contradiction to our recent studies on the higher energy magnon mode ($\omega \sim 27$ cm^{-1}) at ambient pressure [13], where we have clearly shown that this magnon mode exists at temperatures up to $T_{\alpha,\beta}$. To resolve this contradiction [12, 13], one has to re-examine this magnon mode near the α–β phase transition for $p > 0$ GPa.

An additional phenomenon of α-O_2 is intimately connected with its magnetism: two-libron excitations have been observed in our recent zero-pressure Raman measurements [14], which we explained in terms of magnetic coupling of two molecules in the primitive cell performing librations. At first glance, applying pressure, i.e. reducing the distance between neighbouring magnetic molecules, should increase this magnetic coupling. Therefore, the pressure dependences of the frequencies and intensities of these two-libron excitations have to be investigated to obtain information about anharmonicities in the related libron potential, especially as regards the spin dependent contribution.

The general aim of our study is to reinvestigate the low temperature, low pressure region of the antiferromagnetic α phase of solid oxygen, and to clarify ambiguities, e.g. as regards possible phase transitions (discrepancies in the literature), p and T dependences of the higher energy magnon mode and magnetic coupling of libron excitations.

2. Experimental details

A membrane anvil cell was used to generate and vary low pressures (up to 1.25 GPa) with high accuracy ($\Delta p = \pm 0,02$ GPa). This cell, originally equipped with diamonds, was provided with sapphire anvils (10 mm in height, 2 mm culet diameter) and a copper gasket. A few ruby chips were inserted into the sample space to measure local pressure via the frequency shift of the R_1 ruby fluorescence band. The oxygen gas (purity 99.998%) was loaded into the high pressure cell by means of cryogenic loading. Initially, the sample dimensions were 300 μm diameter and 270 μm thickness. The temperature of the sample was determined by a calibrated silicon diode mounted very close to one of the sapphires. The uncertainty of the sample temperature was less than ± 1 K, checked by taking Stokes and anti-Stokes spectra. Raman spectra were excited by the 488 nm or the 514.5 nm lines of an Ar^+ laser at 200–300 mW on the sample and registered by a triple spectrometer (Jobin-Yvon T64000) in conjunction with a charge-coupled device camera. Libron and magnon spectra were measured in the subtractive mode with a resolution better than 2 cm^{-1} and a frequency accuracy of $\sim$0.5 cm^{-1} due to the well known frequencies of atomic lines of Ne, Ar or Kr used for calibration in each spectral run. To obtain good polycrystalline samples for optical investigations, the cooling process from liquid to α phase has been performed extremely slowly ($\sim$1 K h^{-1}). The solid sample was annealed slightly below the crystallization point for about 10–20 h, and we realized again a very slow cooling rate ($\sim$0.1 K h^{-1}) in each phase transition region ($\gamma \rightarrow \beta, \beta \rightarrow \alpha$). Spectra were taken during cooling and warming to allow statements to be made about hysteresis effects and the thermodynamic situation.

3. Spectroscopic results and discussion

We measured vibron (as control), libron, two-libron and magnon excitations along six isobars (0.05, 0.10, 0.35, 0.50, 0.60 and 1.25 GPa) in the α phase of solid oxygen. Pressure was changed only in the high temperature range of the β phase to allow crystal annealing to achieve good optical quality. In the following we will present spectroscopic results of these Raman

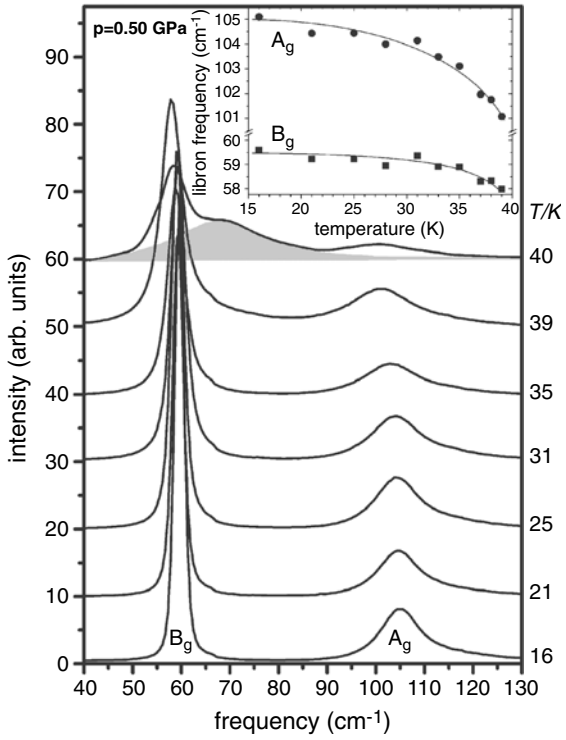

Figure 2. Libron spectra of the α phase at $p = 0.50$ GPa at different temperatures. The two oxygen phases (α and β) coexist in the spectrum at $T = 40$ K. The contribution of the E_g libron in the β phase ($\sim$70 cm^{-1}) is shown in grey, for clarity. The inset presents the temperature evolution of the libron frequencies.

studies and discuss some specific physical aspects in more detail. This section is divided into four subsections: libron modes, two-libron excitations, higher energy magnon modes and a discussion of phase transitions with respect to recent structural investigations contradicting former optical studies.

3.1. Libron modes and mechanical anharmonicities

Both known libron peaks of the α phase at ambient pressure are also present in the Raman spectra in the pressure range investigated. The observed pressure shifts between 0 and 1.25 GPa are

$$\left.\frac{\mathrm{d}\omega}{\mathrm{d}p}\right|_{T=16\ \mathrm{K}} \approx +40\ \mathrm{cm}^{-1}\ \mathrm{GPa}^{-1} \qquad (\mathrm{A_g\ libron})$$

and

$$\left.\frac{\mathrm{d}\omega}{\mathrm{d}p}\right|_{T=16\ \mathrm{K}} \approx +26\ \mathrm{cm}^{-1}\ \mathrm{GPa}^{-1} \qquad (\mathrm{B_g\ libron}),$$

which are steeper at lower pressure. This observation is in accordance with earlier measurements [7–9, 11, 12].

Temperature dependent libron spectra along the 0.5 GPa isobar are shown in figure 2. The spectra look similar for all temperatures with the exception of the one at 40 K, which shows the coexistence of A_g and B_g librons in α-O_2 with the broad E_g libron in β-O_2 (grey area). From

Table 1. Libron frequencies as a function of temperature for three selected pressures in the α phase; all values are in $cm^{-1}\ K^{-1}$. The measured values are given by $\frac{d\omega}{dT}$ which are the sums of implicit contributions ($\frac{\partial\omega}{\partial V}|_T \frac{\partial V}{\partial T}|_p$) and explicit contributions ($\frac{\partial\omega}{\partial T}|_V$).

	$\frac{d\omega}{dT}$		$\frac{\partial\omega}{\partial V}\big\vert_T \frac{\partial V}{\partial T}\big\vert_p$		$\frac{\partial\omega}{\partial T}\big\vert_V$	
Pressure (GPa)	A_g	B_g	A_g	B_g	A_g	B_g
$p \approx 0$ [a]	−0.45	−0.15	−0.45	−0.15	±0	±0
$p = 0.50$	−0.18	−0.06	−0.45	−0.15	+0.27	+0.09
$p = 1.25$	−0.12	−0.04	−0.45	−0.15	+0.33	+0.11

[a] Values from [14].

figure 2 one can distinguish two qualities of libron modes inside α-O_2 as usual: frequency shifts to lower energies and line broadening during sample heating.

In principle, there are two contributions to the total measured temperature shift of one mode frequency $d\omega(T, V(T))/dT$ at constant pressure:

$$\frac{d\omega}{dT} = \frac{\partial\omega}{\partial V}\bigg|_T \frac{\partial V}{\partial T}\bigg|_p + \frac{\partial\omega}{\partial T}\bigg|_V. \tag{1}$$

The first is a shift due to the volume change with temperature (implicit term) and the second a pure temperature shift at constant volume that originates from phonon–phonon interactions (explicit term). At zero pressure (see the corresponding row in table 1) we have shown that the explicit term plays almost no role [14]. Since $\partial V/\partial T|_p$ is almost the same for all small pressures here, the implicit contribution to the frequency shift can be assumed to be of the same value for all pressures. Differences between total and implicit values in the first columns deliver the explicit contribution—given in the last columns of table 1. These results show that the explicit contributions to the frequency shifts become more important with increasing pressure. This means that potential anharmonicities, i.e. phonon–phonon interactions, become more important at higher pressure.

In all the spectra the librons possess a Voigt profile, whose bandwidths (FWHM) we deduced as a function of temperature in figure 3 for four isobars. At lowest temperature the measured bandwidths are the same for all pressures used. The higher the pressure, the smaller the variation of the FWHM with rising temperature. A detailed analysis of the Lorentzian contribution to the bandwidth allows us to make a statement about the pressure dependence of the phonon relaxation mechanisms, known as dephasing and depopulation mechanisms [15, 16]. The probability of elastic libron scattering with bath phonons declines, whereas three-phonon-down depopulation processes become more probable with increasing pressure. Due to theory of mode relaxation, measured bandwidths $\Gamma(T, p)$ are expressed in terms of coupling constants B, which are themselves expressed in terms of changes in the appropriate potential. In our case, increase in the effective phonon coupling constants B is responsible for pressure induced changes in the depopulation process. Therefore we conclude that measured changes in bandwidth with temperature and pressure must be related to potential anharmonicities, i.e. phonon–phonon interactions, which are more important at higher pressures.

In summary, the two well known librons of α-O_2 exist over the whole p–T range under investigation. We measured libron frequency shifts for several isobars as well as the libron bandwidth as a function of pressure and temperature. Both spectroscopic libron characteristics as a function of increasing pressure could be explained by an increase of anharmonicity of the libron potential.

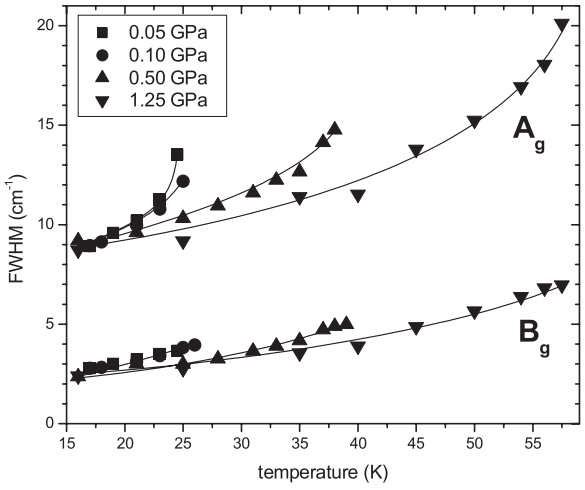

Figure 3. Measured bandwidths (FWHM) of libron excitations at several isobars in the α phase as a function of temperature. (Curves are guides to the eye only.)

3.2. Two-libron excitations

Libron spectra showed either asymmetric band shapes or additional weak bands at higher frequencies at zero pressure [14]. For example, the asymmetry on the high energy side of the A_g libron has been interpreted as a two-libron excitation $B_g + B_g$. This asymmetry was also detected here in all spectra at low pressure. Figure 4 shows a zoom-in view ($\times 100$) of the low energy spectrum and the result of fitting Voigt profiles to the experimental data at 1.25 GPa and 16 K. Besides the two well known librons (dashed curves, $\sim$75 and $\sim$130 cm^{-1}) and the magnon excitation (dotted curve, $\sim$43 cm^{-1}) three additional broad features are visible (solid curves) with maxima at $\sim$140, $\sim$185 and $\sim$260 cm^{-1} which we assigned to the two-libron excitations B_g+B_g, B_g+A_g and A_g+A_g. These two-libron excitations are enabled—according to arguments in [14]—only by magnetic coupling of molecules performing librations. While the intensities of the libron modes are almost the same for all measured temperatures and pressures in the α phase, the intensities of two-libron excitations increase remarkably with pressure (by a factor of five in the pressure range investigated). One can explain this qualitatively by the strengthening of magnetic coupling due to the reduction of intermolecular distances by application of pressure. (The magnetic exchange parameter $J(R)$ increases in this pressure range by a factor of three—using equation (5) and R values in table 2.)

In figure 5 we present the pressure dependences of the frequencies of B_g and A_g librons (ω_{B_g}, ω_{A_g}) as well as those of the frequencies of two-libron excitations ($\omega_{B_g+B_g}$, $\omega_{B_g+A_g}$ and $\omega_{A_g+A_g}$), using different symbols. The simple sums of the ground state frequencies are shown by dotted lines: $\omega_{B_g} + \omega_{B_g}$, $\omega_{B_g} + \omega_{A_g}$ and $\omega_{A_g} + \omega_{A_g}$. At very low pressures (p = 0–0.1 GPa), measured and calculated frequencies coincide quite well. At higher pressures, only the frequency of the two-libron excitation $A_g + A_g$ corresponds to two times the frequency of the A_g libron, i.e. $\omega_{A_g+A_g} \approx \omega_{A_g} + \omega_{A_g}$. In the case of the $B_g + B_g$ two-libron excitation, the measured frequency is lower than two times value for the B_g libron frequency, i.e. $\omega_{B_g+B_g} - \omega_{B_g} - \omega_{B_g} \approx -10$ cm^{-1}. And the observed frequency of the $B_g + A_g$ two-libron excitation is much lower in comparison with the sum of the B_g and A_g libron frequencies: $\omega_{B_g+A_g} - \omega_{B_g} - \omega_{A_g} \approx -20$ cm^{-1} at 0.50 GPa and also at 1.25 GPa.

To explain this behaviour, one has to take into account at least two effects. The first one is the possible dispersion of the libron excitations, and the second one is the anharmonicity of the intermolecular potential.

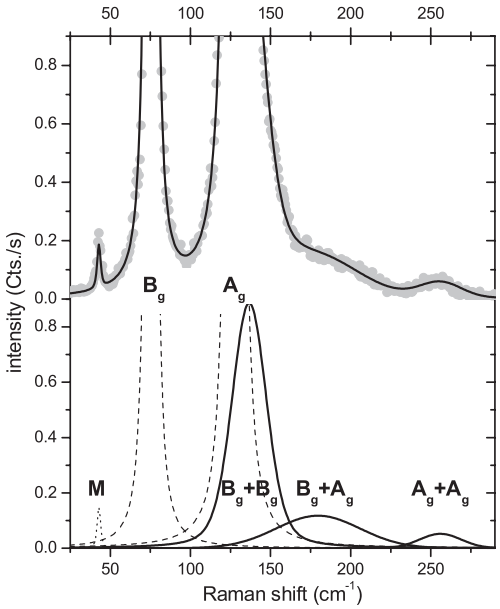

Figure 4. The oxygen spectrum in the low energy range at $p = 1.25$ GPa and $T = 16$ K. The measured spectrum is shown by light grey symbols and its fit by a thick solid curve in the upper part. Single contributions to this fit are shown by different lines in the lower part: libron modes are marked by dashed curves, the magnon mode by a dotted curve and two-libron excitations by thin solid curves.

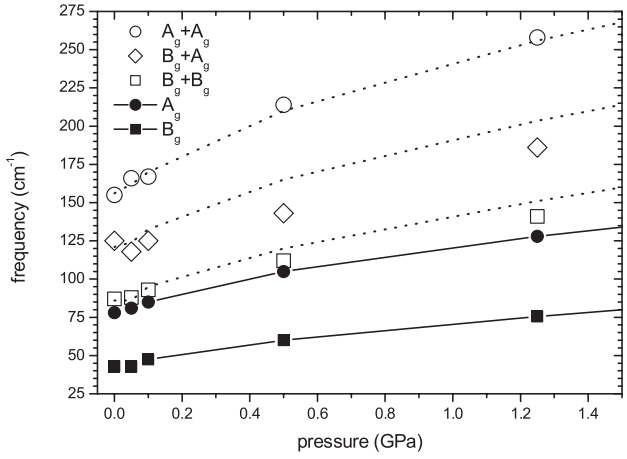

Figure 5. Frequency shift of libron excitations in the low pressure α phase as a function of pressure at $T = 16$ K. Measured data are plotted with closed symbols for librons and with open symbols for two-libron excitations. Dotted lines represent frequencies which result from simple addition of frequencies from librational ground states.

Jansen and van der Avoird [17] calculated the appropriate experimental libron frequencies at the centre of the Brillouin zone, adding a spin dependent term (product of exchange part J and spin–spin correlation function $\langle S_i S_j \rangle$) to the anisotropic libron potential V_{anis}:

$$V_{\text{anis}} = U_{\text{anis}}(\Omega_i, \Omega_j, R) + J_{\text{anis}}(\Omega_i, \Omega_j, R) \cdot \langle S_i S_j \rangle \tag{2}$$

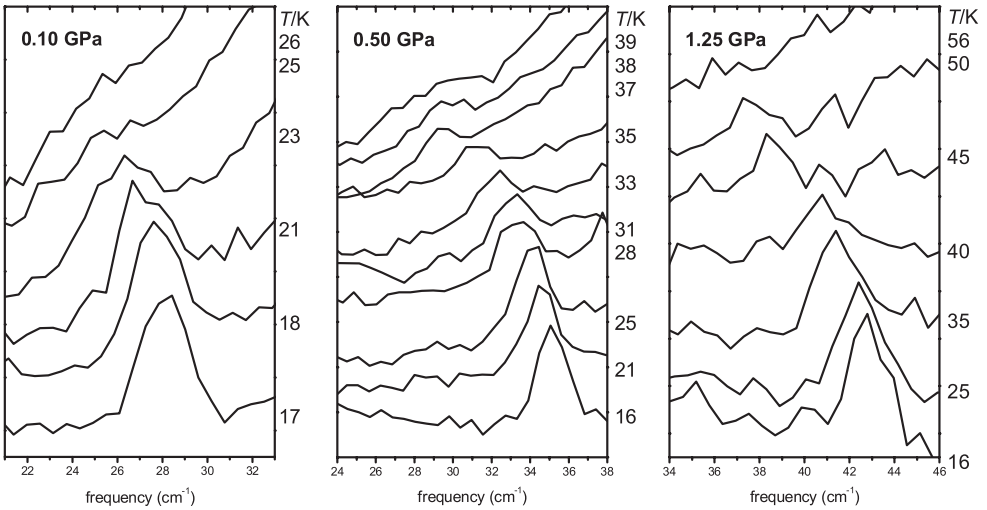

Figure 6. The evolution of magnon Raman spectra in α-O_2 with increasing temperature at three different pressures. (The intensities are differently scaled for the three isobars.)

Table 2. The distance between two nearest neighbours R, the scaled frequency ω/C according to equation (7), the resulting magnon frequency at low temperature $\tilde{\omega}$, the experimental magnon frequency $\bar{\omega}$ and the resulting sublattice magnetization σ_0 at three selected pressures for low temperatures ($T < 20$ K).

p (GPa)	R (Å)	ω/C	$\tilde{\omega}$ [a] (cm^{-1})	$\bar{\omega}$ (cm^{-1})	σ_0
0	3.186	0.1762	27.2	27.2	1
0.5	3.051	0.2424	37.4	35.0	0.94
1.25	2.918	0.3329	51.4	43.0	0.84

[a] Relative to $\omega(p = 0) = 27.2$ cm^{-1}.

where Ω_i, Ω_j are unit vectors along the molecular axis and R is the vector joining the molecular centres [17–19]. We will take the simple average of values at the centre and at the boundary of the Brillouin zone from [17] to estimate the frequency shift due to dispersion. So we get for the A_g libron $\Delta\omega_{A_g}^{disp} \approx +14$ cm^{-1} and for the B_g libron $\Delta\omega_{B_g}^{disp} \approx +25$ cm^{-1}. For the differences in frequencies, that deliver the frequency shifts caused by potential anharmonicities (e.g. $\omega_{B_g+B_g} - 2\omega_{B_g} - 2\Delta\omega_{B_g}^{disp}$), we get ~ -60 cm^{-1} for $B_g + B_g$, ~ -49 cm^{-1} for $B_g + A_g$ and ~ -28 cm^{-1} for $A_g + A_g$. Hence, the anharmonicity of the potential for the B_g libron is more important than that of the potential for the A_g libron.

In conclusion, we have analysed the intensities and frequencies of two-libron excitations. The increase in intensity for two-libron excitations with increasing pressure can be qualitatively explained by an increase of the magnetic coupling between librating molecules in α-O_2 due to the decrease in distance between them. The influence of the anharmonicity of the libron potential has already been pointed out for libron spectra (section 3.1). Therefore, the changes of the frequencies of two-libron excitations with increasing pressure are also related to these potential anharmonicities, which are stronger for the B_g libron than for the A_g libron.

3.3. Higher energy magnon mode and magnetic properties

Figure 6 illustrates the temperature evolution of the Raman spectra of the higher energy magnon mode at three selected isobars. The general behaviour at pressures $p > 0$ GPa is the same as

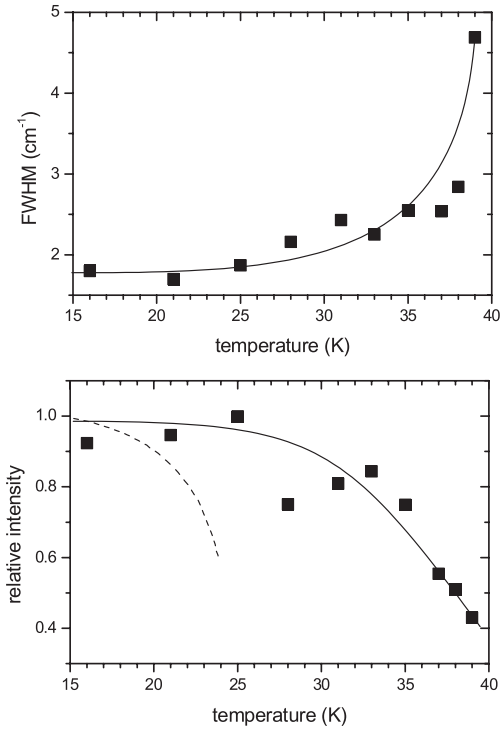

Figure 7. The bandwidth and relative intensity of the higher energy magnon mode as a function of temperature along the 0.50 GPa isobar. The intensities are given relative to the constant intensity of the A_g libron mode; the maximum is scaled to the value 1. The dashed curve shows $I(T)$ for $p = 0$ [14]. (Solid curves are guides to the eye.)

for ambient pressure [13]: during heating, the band frequency decreases and the bandwidth increases. Since the bandwidth increases, the amplitude must of course decrease. The magnon bandwidth rises by a factor of less than three; therefore its amplitude should be about one third of that at 16 K (under the assumption that the intensity is constant). However, it is even less; thus one can conclude that the intensity of the magnon mode decreases with increasing temperature.

But the question is now whether the integrated intensity as a function of p is constant or decreases too—which would not be expected due to the magnetic origin of this excitation. In fact, one would expect an increase in magnon intensity I with rising pressure: $I \sim J(R)$. The noise in all spectra presented here is at the same level; therefore the signal to noise ratio in spectra at 16 K decreases with increasing pressure and the intensity of the magnon mode decreases. In consequence, the magnon peak at 1.25 GPa is detectable only up to a temperature of 45 K, possibly also up to $T = 50$ K. However, one cannot observe the magnon up to the α–β phase transition at $T_{\alpha,\beta} \approx 57$ K in our spectra at 1.25 GPa. We attribute this disappearance of the magnon mode to the limit of sensitivity of our system and not to changes in principle of the magnetic structure of α oxygen.

Figure 7 presents the bandwidth and relative intensity (relative to intensity of the A_g libron and scaled to 1 at $T = 0$ K) of the higher energy magnon mode at the 0.50 GPa isobar. The bandwidth shows a temperature dependence, which is larger than a power of 4—as in the case of $p = 0$ GPa. Since the errors of the bandwidths are relatively large ($\sim$0.5 cm^{-1}), a more detailed evaluation is not possible.

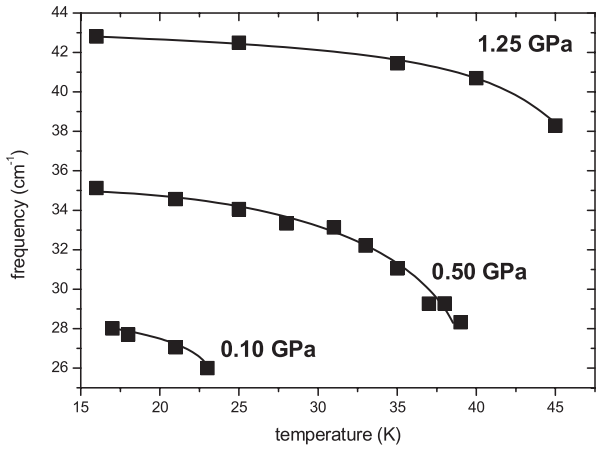

Figure 8. The dependence of the frequency of the higher energy magnon mode for three selected isobars on temperature.

The relative intensity of the magnon mode decreases with increasing temperature (figure 7, lower part). While the relative intensity is ∼0.6 for $p = 0$ GPa [13] near the α–β phase transition in comparison with the intensity at the lowest temperature, it is only ∼0.4 at $p = 0.5$ GPa—but the temperature is more than 1.6 times higher in the latter case. These observations indicate that the physical processes are the same in this p–T range; only the limits of the parameters are different. This result is clearly in contradiction to the statement of Mita *et al* [12] that a magnetic phase transition occurs at temperatures lower than $T_{\alpha,\beta}$.

The temperature and pressure dependence of the magnon frequency at three isobars is shown in figure 8. The frequency softening with increasing temperature is caused by the volume dependent exchange field and the temperature dependent sublattice magnetization. The antiferromagnetic resonance mode frequency in α-O_2 at the centre of the Brillouin zone is given in the mean field approximation by (see e.g. equation (30) in [20])

$$\omega(T, R) \sim \sqrt{4AJ(R)(\sigma(T))^2}\,, \tag{3}$$

where A is the anisotropy constant, σ is the sublattice magnetization $\langle S_i S_j \rangle$ (the magnetic order parameter, which is temperature (T) but not directly distance (R) dependent) and $J(R)$ is the exchange field. Now let us consider this situation in the case of low temperatures and non-zero pressure. In the limit $T \to 0$ equation (3) simplifies to

$$\omega(R) \sim \sqrt{4AJ(R)\sigma_0^2}. \tag{4}$$

The exchange interaction $J(R)$ can be described by the expression

$$J(R) = J_0 \exp[-\alpha(R - R_0)], \tag{5}$$

where $J_0 = 19.6\ \mathrm{cm}^{-1}$, $\alpha = 3.765\ \text{Å}^{-1}$ and $R_0 = 3.187$ Å [21]. Following the arguments of Freiman [1], the in-plane anisotropy A can be compared with the magnetic dipole energy

$$E_{\mathrm{dipole}} \sim \frac{1}{R^3}. \tag{6}$$

With expressions (5) and (6) and the preliminary assumption that σ_0 is not a function of pressure, equation (4) becomes

$$\omega(R) = C\sqrt{\frac{1}{R^3}\exp[-3.765\ \text{Å}^{-1}(R - 3.187\ \text{Å})]}, \tag{7}$$

where C is a constant. The distances between the nearest neighbours $R(p)$, shown in table 2, are obtained from lattice parameters at $T = 19$ K [5]. Then, the values for $\omega(R)/C$ (which are shown in the next column in the table) are derived with help of equation (7). Since the magnon frequency at low temperatures and zero pressure is 27.2 cm^{-1} [13], we can calculate (from the $\omega(R)/C$ results) the frequency $\tilde{\omega}$ which contains the R dependences of the exchange interaction J and of the anisotropy 'constant' A. Finally, the ratio of experimentally determined frequencies to calculated ones then delivers directly the sublattice magnetization as a function of pressure:

$$\sigma_0(p) = \frac{\bar{\omega}(p)}{\tilde{\omega}(p)}. \tag{8}$$

Since a possible pressure dependence of the sublattice magnetization $\sigma = \langle S_i S_j \rangle$ was neither experimentally nor theoretically investigated, it is difficult to extrapolate $\sigma(p)$ to a critical pressure where it becomes zero, i.e. where the antiferromagnetic order disappears. But these three σ values determined (table 2) lie on a straight line: $\sigma(p) = 1 - p \cdot 0.13\,\mathrm{GPa}^{-1}$. As a first assumption, a linear extrapolation yields $p_{\mathrm{crit}} \approx 7.7$ GPa for $\sigma \to 0$. Surprisingly, this is near the pressure of the phase transition from the high pressure antiferromagnetic δ phase to the non-magnetic ε phase [6].

This result, $\sigma(p) \to 0$ with $p_{\mathrm{crit}} \sim 7.7$ GPa, contradicts the former statement by Mita *et al* [12] that magnetic order has already disappeared at pressures larger than ~2.9 GPa, due to vanishing magnon intensities in their Raman spectra in this pressure range at $T = 1.8$ K. But another conclusion from vanishing magnon intensities might be that the authors 'destroyed' their samples, because they varied the pressure at 1.8 K and, consequently, the samples may scatter much more incident laser light. To check this hypothesis we compare the magnon intensities in figure 9, as a function of pressure, obtained by two different procedures, applying pressure: the Mita *et al* data obtained at the 1.8 K isotherm (open squares) and actual data obtained at 16 K for different pressures after isobaric cooling from the β phase (solid circles). Since there is almost no difference between the data sets, we believe that the effect of crystal quality on the variation of the magnon mode intensity by pressure to be negligible for the data reported by Mita *et al*. This large pressure dependence must be mainly caused by another effect. But since we can exclude the possibility of an influence from J and σ, we are not able to say which effect is responsible for the drastic decrease.

To conclude, the frequency, bandwidth and intensity of the higher energy magnon mode show basically the same temperature behaviours at elevated pressures, like at ambient pressure. At 0.5 GPa we demonstrated that this magnon mode still exists up to the temperatures of the α–β phase transition—in contradiction to reports by Mita *et al*. Pressure dependent magnon frequencies allow us to estimate the sublattice magnetization σ as a function of pressure. An (admittedly risky) extrapolation makes a determination of the critical pressure possible; here the magnetic order disappears: ~7.7 GPa. In that pressure range at low temperatures several authors [5, 6, 22] found the α or δ (antiferromagnetic) to ε (non-magnetic) phase transition. Our result contradicts the statement of Mita *et al*, who estimated a phase transition (magnetic → non-magnetic) at ~2.9 GPa. Therefore, on the basis of our present magnon results, a previously suggested phase transition with varying temperature can be ruled out and considerable doubt is cast on another reported with varying pressure. In the next section we will critically discuss all other reported phase transitions in the low temperature, low pressure range of solid oxygen.

3.4. Phase transitions from Raman spectra

In the introduction we mentioned all possible phase transitions in the low pressure, low temperature range which different authors claimed to exist according to small changes in

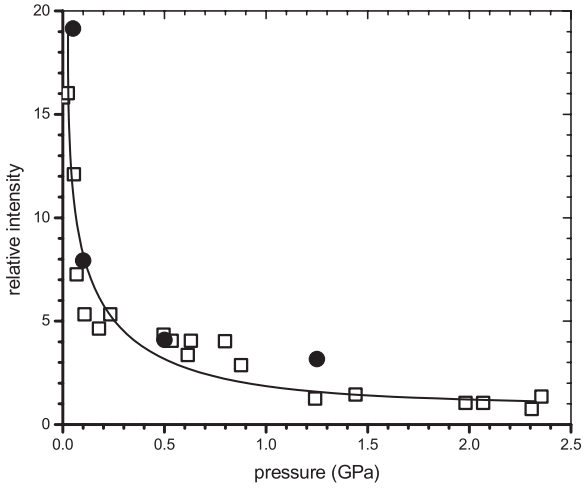

Figure 9. Intensity of the high energy magnon mode versus pressure, scaled with respect to the intensity of the A_g libron mode ($10^3 \times I_{\mathrm{magnon}}/I_{A_g-\mathrm{libron}}$) at the same conditions. Open squares are data from [12], obtained at the 1.8 K isotherm. Solid circles are the actual data at 16 K, obtained by isobaric cooling from the β phase. (The solid curve is a guide to the eye.)

Raman spectra of vibron, libron and magnon modes—see also figure 1. We have already ruled out, in section 3.3, two magnetic phase transitions within the structure α-O_2 which were suggested by Mita *et al* [12] due to disappearance of the magnon mode in their spectra. Most groups [7–9, 12] used linear fitting functions to model the pressure dependence of the mode frequencies, as a first guess. Therefore, they suggested (second-order) phase transitions on the basis of small changes in slope of $\omega_i(p)$; but for the physical processes involved, e.g. volume dependences on pressure and anisotropy, fitting functions based on higher order polynomials are much more appropriate. As an example, we demonstrate in figure 10(a) how the authors in [8, 9] deduced—from changes in linear fits to vibron and libron frequencies as a function of pressure—a possible phase transition at 3 GPa. In figure 10(b) we show the fits of frequencies as quadratic functions of pressure. The fitting function corresponds quite well with experimental data. Therefore, one can exclude the possibility of the existence of the suggested phase transition at ∼3.0 GPa [8, 9]—just like the one at ∼0.9 GPa (suggested by Meier *et al* [7]) and the one at ∼1.3 GPa (suggested in [12]).

Now, for comparison, all data from Raman spectra obtained by different authors are collected in figure 11, where we have plotted the frequencies of magnon, libron and vibron excitations as a function of pressure at $T < 20$ K: data from Meier *et al* [7] are represented by full squares at 6 and 18 K, those of Hochheimer and Jodl [8, 9] (10 K) by full circles; frequencies reported by Mita *et al* [12] at 1.8 K are shown as grey diamonds; results from actual Raman studies (16 K), obtained by isobaric cooling, are symbolized by stars. Due to obvious systematic errors in determination of absolute frequency positions, we shifted Meier's data for 0.6 cm^{-1} to lower frequencies and Hochheimer's and Jodl's data for 0.5 cm^{-1} to higher frequencies. With respect to our fitting functions (solid lines), the different values of $\omega_i(p)$ scatter less than ± 0.5 cm^{-1} for vibrons, ± 2 cm^{-1} for librons and ± 1 cm^{-1} for magnons. Only in the pressure range 0.2–0.5 GPa do the data obtained by Hochheimer and Jodl deviate more than other values from the solid lines. By (fast) pressing of the sample at 10 K, one produces stress and strain in the sample. Therefore the frequencies lie at higher values than they would in the case of a sample under thermodynamically stable conditions. At a certain pressure, the

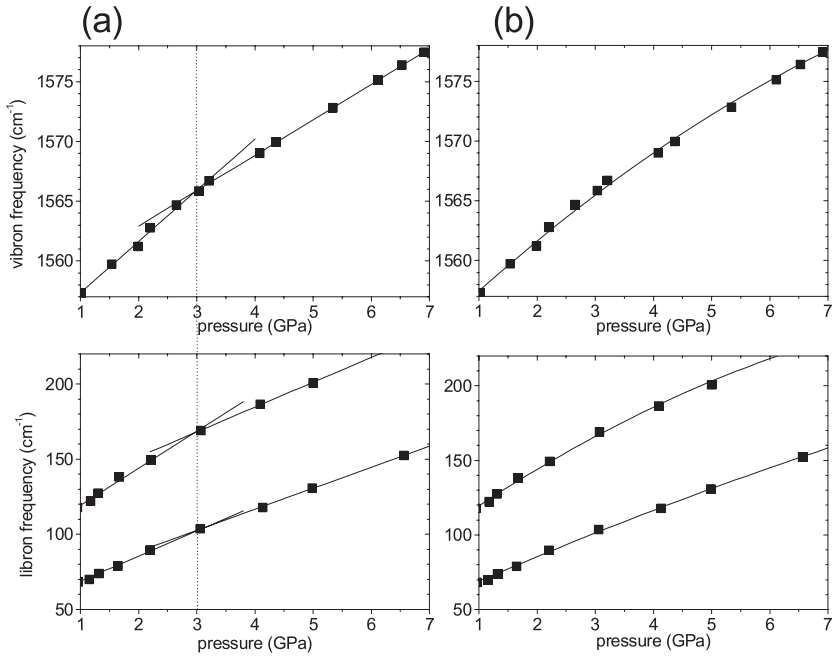

Figure 10. Symbols show frequencies of libron and vibron excitations observed in the Raman experiment by Hochheimer and Jodl at 10 K [8, 9]. Part (a) shows their original fit with two linear sections; part (b) shows our fit with only one quadratic function.

mechanical strain is too high and microscopic parts of the sample relax. Although other groups also changed the pressure at the lowest temperature, they may have performed these changes more slowly; therefore, their $\omega_i(p)$ data do not deviate as much.

According to our critical discussion, only the phase transition that was suggested at $\sim$0.07 GPa by Mita *et al* [12] remains. These authors observed small jumps in frequencies of libron and magnon modes of 0.8–1.8 cm^{-1}. According to their technical information on the spectrometer etc, we presume that the spectral resolution was only about 1 cm^{-1}. Therefore, this suggested phase transition at $\sim$0.07 GPa is questionable. Additionally it is possible that some unstable magnetic phases have been observed in the experiments by Mita *et al*—such as intermediate phases in the region of the α–β phase transition which were reported in [23] and [24] and discussed in [1]. But even if this was the case, the observed results were not detected under thermodynamically stable conditions.

To conclude, one of our aims was to find out whether there is an appreciable difference in data ($\omega_i(p)$) obtained during isothermal compression in the cold state and the data obtained with isobaric cooling. Only if there is a clear jump in frequency or a coexistence of two phases (see the libron spectrum at 40 K in figure 2) can one assign these changes in spectra as due to (first-order) phase transitions. Of course, samples must be under the best thermodynamically stable conditions. According to our comparison of all published Raman data, we suggest a revised p–T diagram of thermodynamically stable solid oxygen, shown in figure 12. As a result of our spectra, there is no phase line in the range of pressures lower than 4 GPa and temperatures lower than β phase. As is the case in Gorelli's structural analysis [6], the δ phase exists at low temperatures in thermodynamically stable samples and also in our Raman experiment at pressures up to 10 GPa [22].

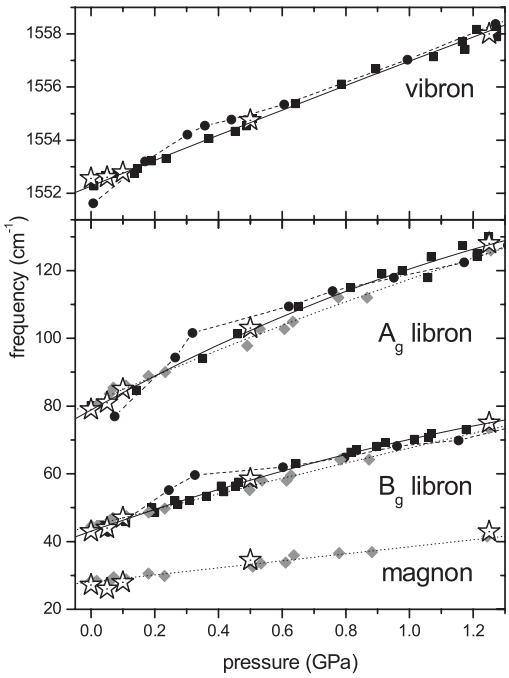

Figure 11. Frequencies of magnon, libron and vibron excitations observed in different Raman experiments: squares at 6 and 18 K [7], circles at 10 K [9], grey diamonds at 1.8 K [12] and stars at 16 K obtained by isobaric cooling in the actual experiment.

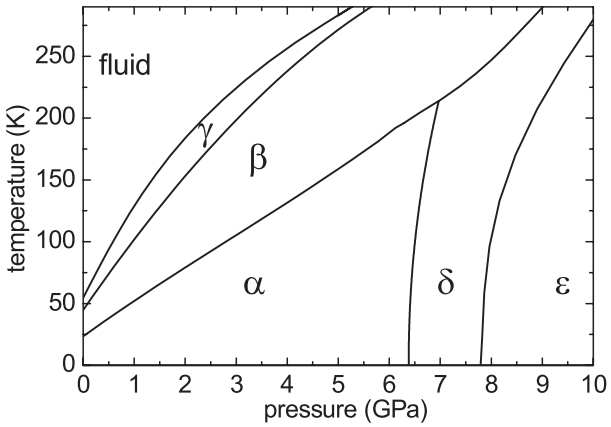

Figure 12. The phase diagram of oxygen up to 300 K and 10 GPa obtained as a result of the current investigations and a structural study [6] as well as a Raman study at higher pressure [22].

4. Conclusion

Raman scattering studies on solid α oxygen have been performed at several isobars in the pressure range up to 1.25 GPa. Pressure was changed only in the high temperature β phase to keep samples at thermodynamical equilibrium and maintain good optical crystal quality. The low lying fundamental excitations such as vibrons, librons and magnons as well as the combined

two-libron excitations have been investigated as a function of pressure and temperature. Since we were able to vary the pressure and temperature separately, we could distinguish between explicit and implicit contributions to frequency shifts of librons; as a result, the phonon–phonon interaction becomes more important at higher pressures. We observed several very weak bands on the higher energy side of the librations, which we assigned to two-libron excitations. In the α phase there are two molecules in the primitive magnetic cell which interact during libration via magnetism. Frequencies of two-libron excitations increase with rising pressure; we found that this potential anharmonicity is more important for the B_g libron than for the A_g libron. Whereas both libron intensities are almost constant for all p–T values investigated, the intensities of two-libron excitations increase by a factor of 5 on applying pressure due to an enhancement of the spin coupling mechanism.

The higher energy magnon mode (at 27 cm^{-1}) shows in principle the same temperature dependent behaviour in ω, Γ and intensity for all isobars investigated. It exists up to $T_{\alpha,\beta}$ even at pressures up to 0.5 GPa. The magnon frequency can be modelled in the mean field approximation by several parameters (A: anisotropy constant; J: exchange field; σ: magnetic order parameter). Since we measured this magnon frequency as a function of pressure and temperature and since we know the R dependence of A and J from the literature, we can give an estimate for the pressure dependent sublattice magnetization $\sigma(p)$. Extrapolating these data to the critical pressure where σ becomes zero, we get a p value of $\sim$7.7 GPa. This pressure value is in agreement with the phase boundary between the antiferromagnetic ordered α or δ phase and the non-magnetic ε phase. As expected, the bandwidth and band amplitude vary upon applying pressure. But, in addition, the magnon intensity decreases drastically with increasing pressure. But since the exchange field J increases with pressure and σ shows only a small dependence on pressure, there must be another effect responsible for the drastic reduction of the magnon intensity with pressure.

The present results suggest that this magnon exists over the whole α phase. Therefore we exclude the possibility of two magnetic phase transitions which have been proposed by Mita *et al* [12]. If we put all known mode frequencies $\omega_i(p)$ at low temperatures from known Raman studies on vibrons, librons and magnons in one diagram—showing ω_i versus pressure—most of these values lie on a quadratic fitting function. In cases where some data deviate more from these fitting functions, we can explain this deviation by (presumably) thermodynamically unstable samples, caused by the pressure being applied at low temperature in these investigations. As a main result of the present investigations, we see that no phase transitions exist in the low temperature, low pressure α phase up to the temperatures of the β phase and the pressures of the δ phase.

Acknowledgments

We gratefully acknowledge a critical reading of our manuscript to B Eckert. This work was supported by the Deutsche Forschungsgemeinschaft (Grant No Jo 86/10-3).

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