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Infrared response of glassy Ar:O_2 mixed crystals

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Solid solutions $Ar_{1-x}(O_2)_x$, $0.2<x<1$, have been investigated by infrared-absorption measurements of the O_2 stretching-band region. The experiments suggest the formation of a quadrupolar and possibly also a spin-glass state with a hcp center-of-mass lattice of $0.3<x<0.6$. [S0163-1829(97)00113-6]

INTRODUCTION

Quadrupolar glasses are systems with a crystalline center-of-mass lattice in which the orientations of the nonspherical, quadrupolar constituent freeze at low temperatures (T) into patterns devoid of long-range orientational order.[1] The freezing process of such systems has been described by spin-glass-type random bond models and alternatively by theories which treat a structural phase transition subject to random fields.[2] On the experimental side the most insight into quadrupolar freezing has been obtained for cyanide mixed crystals such as KBr:KCN, solid solutions of ortho-para-H_2 and Ar:N_2. Ar:O_2 has several similarities with Ar:N_2. The shape and the size of the N_2 and the O_2 molecules are about the same. In particular, for intermediate concentrations x both systems show a hcp phase with dynamical orientational disorder.[3,4] The c/a ratio of this phase is close to the ideal value of a close packing of spheres. This suggests that the average quadrupole moment not only vanishes within the basal plane but also along the c axis. In both systems the hcp phase can be supercooled to lowest temperatures. Here we study the freezing of Ar:O_2 by means of infrared (IR) spectroscopy of the stretching-band region. We have previously applied this method to Ar:N_2.[5,6] In contrast to N_2, the O_2 molecule carries a magnetic moment, which is perpendicular to the molecular axis.[14] Thus one expects that the quadrupolar and magnetic degrees-of-freedom are not independent of one another and that both magnetic and quadrupolar interactions are active in orientational ordering. Obviously such a coupling of magnetic and structural degrees of freedom is present in pure O_2, where the structural phase transitions at 44 K (γ-β) and 24 K (β-α) are accompanied if not driven by changes of the magnetic structure:[14,15,27] in the paramagnetic γ phase ($Pm3n$), O_2 occupies two different lattice sites with planar, respectively, spherical disorder of the molecular axis. In the β phase ($R3m$) the molecules are oriented parallel to the c axis, and antiferromagnetic short-range order is observed. In the corresponding ordered magnetic structure the spins form a 120° structure in the ab plane and show antiparallel order in adjacent ab planes. In the α phase, magnetic long-range order into a simple two-sublattice antiferromagnet is established, and the structure becomes monoclinic ($C2/m$).

The x, T phase diagrams of Ar:O_2 solid solutions have been investigated by Barrett, Meyer, and Wasserman,[3] by Prokhvatilov and Baryl'nik,[7] and by Ahmad, Kiefte, and Clouter.[8] The authors agree approximately on the high-temperature part of the diagram but differ considerably on the low-T part. According to Barrett, Meyer, and Wasserman and Ahmad, Kiefte, and Clouter the hcp phase is stable down to the lowest T for $0.2<x<0.5$. For $0.5<x<0.8$ Barrett, Meyer, and Wasserman report the so-called δ phase (a superstructure of the γ phase[9]), and for $x>0.9$ the α phase. On the other hand, Prokhvatilov and Baryl'nik suggest that at low T the only stable structures are the Ar-rich fcc phase for $x<0.4$ and the α phase of practically pure O_2. According to these authors solid solutions with $0.2<x<0.4$ should transform from hcp to fcc at 40 K. However, they point out that the hcp phase can be supercooled by sufficient fast cooling. Because of these discrepancies an investigation of the full range of O_2 concentrations from 0.2 to 1 was required. Nevertheless, our main interest focuses on the range $0.3<x<0.6$ where our samples stay hcp down to lowest temperatures and form a glassy state.

The present experiment probes the IR response of the O-O stretching band. Of course, the fundamental vibration is IR forbidden for the free molecule. Both experiment and factor-group analysis agree on the fact that the O_2 fundamental is also forbidden in the α and β phases of solid pure O_2.[10] The situation in the dynamically disordered γ phase of O_2 is less obvious from the symmetry point of view. In any case the present experiment suggests that here, too, the fundamental is IR forbidden. Thus all the IR absorbance of the stretching region in the solid phases of pure O_2 is due to two-excitation processes $[\nu_{\mathrm{vib}}(k)\pm\nu_{\mathrm{phon}}(-k)]$, one excitation being the stretching vibration, the other one a lattice mode (phonons and magnons of the center-of-mass lattice and orientational excitations such as librations or diffusive reorientations). Assuming that the width and the dispersion of the vibron are negligible, the sideband structure can therefore be regarded as a density of states of the lattice modes weighted with the thermal population factor and the mode-dependent coupling coefficient for IR absorption.[11] In addition, the direct absorption process at the vibron frequency can be induced in a perturbed local environment, such as lattice point defects, stacking faults, grain, phase, and domain boundaries.

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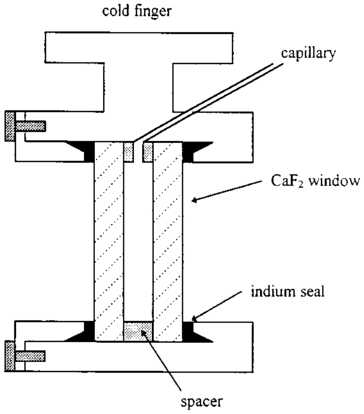

FIG. 1. Schematic view of the sample cell used for the FTIR experiments.

EXPERIMENTAL

Appropriate quantities of the gases Ar and O_2 with nominal purities of $6N$ and $5N$, respectively, have been portioned and mixed in an all-metal gas handling system equipped with a 1000 mbar pressure gauge. The gas is condensed into a copper sample cell (Fig. 1), equipped with two CaF_2 windows and attached to the cold plate of a closed-cycle refrigerator. The thickness of the sample between the CaF_2 windows is 0.6 mm. In total we investigated solid solutions $Ar_{1-x}(O_2)_x$ with 14 different O_2 concentrations ranging from $x=0.2$ to pure O_2 $(x=1)$. As there is evidence from the work of other authors that the structures and the excitations of the samples depend on the thermal history and preparation of the samples,[3,7,8,12,13] we treated all samples in exactly the same way which we established in exploratory measurements: The liquid mixtures were allowed to settle for several hours and then were cooled down through the liquid-solid coexistence region with the maximum cooling rate of the closed-cycle refrigerator (3 K per min). Subsequently they were annealed for at least 2 h about 5 K below the solidus line for homogenization. Visual inspection, either directly or through crossed polarizers, suggests that cracks or inhomogeneities heal out within a few minutes at these high temperatures. A first IR measurement is then recorded at 50 K, the following ones every full degree K on cooling down to 10 K. The whole sequence is reversed on heating back to 50 K. The cycle is performed within 8 h, hence the effective heating and cooling rate is about 0.2 K per min. In pure O_2, we obtain visually transparent single crystals in the γ phase, characterized by high IR transmission. At the β-γ structural phase transition the sample transforms into a polycrystalline state with very low IR transmission. The sample being visually opaque we derive grain sizes of about the wavelength of visible light. In the hcp mixtures the IR transmission decreases gradually but remains much higher than in the β phase, the formerly transparent samples now become only translucent.

The IR absorption spectra have been measured with a Fourier-transform infrared (FTIR) spectrometer (Perkin Elmer System 2000). The spectral resolution was set to 0.5 cm^{-1}.

RESULTS AND DISCUSSION

A. Pure O_2

Figure 2 gives an overview of the various types of spectra of the stretching-band region which have been observed as a function of T and x. The spectra of the α and β phases of pure O_2 are known from measurements of previous authors.[10,11] They observed traces of the O_2 fundamental ν_{vib} at frequencies around 1550 cm^{-1}. As the intensity of this absorption line depends on preparation and annealing, the presence of the fundamental has been attributed to defects in the sample.[10] With our type of preparation and annealing we were able to suppress the fundamental in the spectra of the low-T solid phases of pure O_2 $(x=1.0)$ completely. We take this as an indication that our samples are of high quality. As mentioned above the sideband can be interpreted as a weighted density of states $g(\nu')$ of the lattice modes $\nu'=\nu-\nu_{\mathrm{vib}}$. Because of the low temperature, $g(\nu')$ mainly shows up on the Stokes side of the band origin at $\nu=\nu_{\mathrm{vib}}$. Attempts have been made to relate the various features of the sideband of the α and β phases to special lattice modes.[11] The α and the β phases have closely related

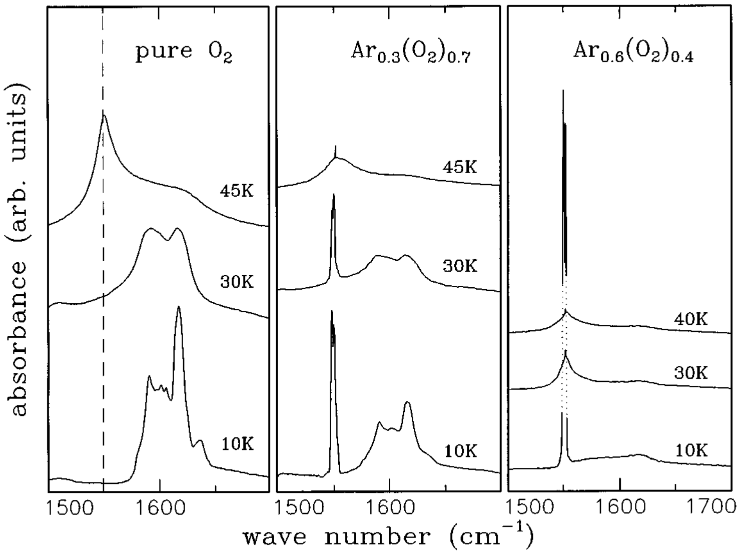

FIG. 2. IR absorbance spectra of the stretching-band region for selected temperatures and composition.

crystallographic structures,[3] hence $g(\nu')$ is similar in the two phases. Nevertheless there are two particular features which can be used to discriminate the α phase from the β phase what in turn allows us to specify the α-β-transition temperature: (i) the maximum at $\nu' = 85\ \mathrm{cm}^{-1}$, which is likely to be due to magnetic excitations of the antiferromagnetically ordered α phase: the spin-flip intensity of inelastic neutron scattering has a maximum at $81\ \mathrm{cm}^{-1}$ in the α phase, indicating a maximum in the magnon density of states, in the β phase this maximum is absent;[14] (ii) the higher density of states in the low ν' range of the β phase, which presumably represents low-lying orientational modes. The transition from the β phase into the γ phase leads to a drastic change of the sideband spectrum. The stretching-band region of the γ phase is dominated by a quasielastic Lorentzian-like component, centered at $\nu' = 0$, which we attribute to overdamped orientational modes, i.e., rotational diffusion, as expected for a phase with dynamic orientational disorder. The residual feature around $\nu' = 70\ \mathrm{cm}^{-1}$ roughly coincides with the cutoff frequency of the low-T phases and may thus mainly represent zone-boundary phonons. The still finite absorption at even higher frequencies ν' is due to higher-order effects.

The changes of the sideband structure propose the α-β transition between 23 and 24 K and the β-γ transition between 43 and 44 K, both on cooling and heating, in agreement with the literature.[3,7,15]

For the presentation of the results on the solid solutions, we divide the concentration range into two parts, namely $0.3 \leqslant x \leqslant 0.6$ and $0.60 < x < 1$. We mention in passing that there is no measurable sideband absorption left for $x = 0.2$, only a weak vibron spike is observed at $1551.9\ \mathrm{cm}^{-1}$.

B. Solid solutions with $0.60<x<1$: The regime of phase separation

For $0.60 < x \leqslant 0.95$ the variation of the sideband structure with temperature is similar to pure O_2 (see Fig. 2), although — as x is reduced — the characteristic structures of the α and the β phases get progressively smeared out. The density of states clearly is a bulk property, therefore we consider the sideband structure as a fingerprint of the sample volume, which is only insignificantly influenced by structural defects. The most natural explanation for the absorption spectra is in terms of a phase coexistence: the sideband is a superposition of the sideband of an O_2-rich α, respectively, β phase and of a smooth, featureless sideband of an Ar-rich phase, the weight of the latter growing at the expense of the former when x is reduced. This postulated phase coexistence agrees with the phase diagram of Prokhvatilov and Baryl'nik. Note however that in our measurements the Ar-rich phase stays hcp down to lowest temperatures without showing any evidence for a transformation into fcc. The sideband gives no evidence for the existence of the low-temperature δ phase which has been observed by Barrett and co-workers for $0.6 < x < 0.8$.[3,9]

The α-β phase transformation of the O_2-rich component takes place between 21 and 22 K, both on cooling and heating, while the transition from the β phase into the high-T phase occurs at about 34 K on cooling and 39 K on heating. These values hold for all samples in the stated x range.

In the high-T regime the sideband structure appears to be independent of the structure of the center-of-mass lattice. No matter whether the sample is in an x,T state which corresponds according to the phase diagrams to a single hcp phase, single γ phase or to a γ-hcp coexistence state, the sideband is dominated by the broad quasielastic component centered at $\nu' = 0$ which has already been observed in pure γ-O_2 (Fig. 2).

In the concentration regime $0.60 < x < 1$, the intensity and shape of the O_2 fundamental strongly depend on x,T and are different for cooling and heating. The fundamental is almost absent in the initial high-T state immediately after sample preparation but acquires a complex and strong pattern in the T range where the demixing process into β-O_2 and Ar-rich hcp occurs, $39\ \mathrm{K} > T > 33\ \mathrm{K}$. Further changes occur in the T range of the α-β transition. At the end of the thermal cycle when the sample is back in the high-T state, there is considerable residual intensity left. These are clear indications that at least a great deal of the intensity of the O_2 fundamental is due to lattice defects, such as phase boundaries introduced by phase separation. Altogether the various components of the O_2 fundamental cover a ν range 1547 to $1553\ \mathrm{cm}^{-1}$. There is no obvious way how to assign the individual lines to specific phases or defect states. Nevertheless a doublet observed at low T at 1550 and $1552\ \mathrm{cm}^{-1}$ apparently increases with decreasing O_2 concentration. Since this feature is the only one remaining for $x \leqslant 0.6$, it is likely to belong to the hcp low-T state of Ar:O_2. For low T, there is an additional spike at $1548\ \mathrm{cm}^{-1}$ which can be traced from $x = 0.65$ to 0.80. Perhaps this is an indication of residues of the δ phase which has been observed by Barrett *et al.* in about this x range. None of the observed line patterns agrees with the O_2 fundamentals which have been assigned to a metastable phase, called the *m* phase, in evaporated thin O_2 films.[16]

C. Solid solutions with $0.3 \leqslant x \leqslant 0.6$: The glassy regime

In contrast to the spectra of the previous x range, the spectra for $0.3 \leqslant x \leqslant 0.6$ are independent of the thermal history of the sample and change smoothly with x and T, see Figs. 2 and 3 for $x = 0.4$ and 0.5. Apart from the splitting of the fundamental (Fig. 4) there is no evidence for phase transitions or phase separation. The spectra can be split into three elements: the O_2 fundamental, a quasielastic component of about Lorentzian shape and the density of state part. The density of state part is a rather smooth function of ν, the most prominent feature being the maximum, respective, shoulder at $1620\ \mathrm{cm}^{-1}$ which represents lattice modes close to the cutoff frequency. The low-frequency regime of the density of states part is visible at low temperatures only, at higher temperatures the quasielastic component of approximately Lorentzian shape is superimposed. The latter represents relaxing degrees of freedom, the most obvious are reorientations of the O_2 molecules. The Lorentzian width decreases with decreasing temperature (Fig. 5). This narrow-

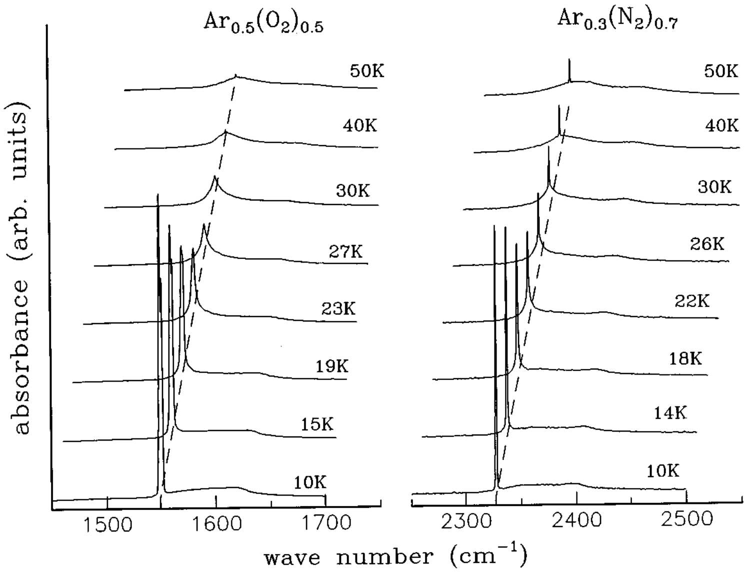

FIG. 3. The temperature evolution of the O_2, respectively, N_2 stretching-band region of $Ar_{0.5}(O_2)_{0.5}$ as compared to that of the well established quadrupolar glass system $Ar_{0.3}(N_2)_{0.7}$ (from Ref. 6). The spectra of either series are offset vertically and horizontally, as indicated for the band origin by the dashed lines.

ing of the quasielastic component signals the gradual freezing of the O_2 orientations.

The fundamental starts out as a tiny spike in the high-T hcp phase, the width given by the instrumental resolution (Figs. 3 and 4). It grows, broadens, and splits on cooling. Ignoring the splitting for the moment, the spectra and their changes with T are very similar to the results on hcp Ar:N_2, as illustrated by the synopsis of Fig. 3. This suggests that Ar:O_2 undergoes a freezing process very much like Ar:N_2. Apart from the narrowing of the quasielastic component, the most conspicuous effect of the freezing is the appearance of the strong IR activity of the fundamental. As for Ar:N_2 we point out that this IR activity cannot simply be a consequence of the substitutional site statistics of a mixed crystal, which in principle could induce IR activity, since then the fundamental should be strong at all, and not only at low temperatures. Neither can it be due to the site symmetry broken by orientations of the neighboring O_2 molecules. As the vibron oscillations are fast compared to the reorientational modes over the entire T range of the present study,

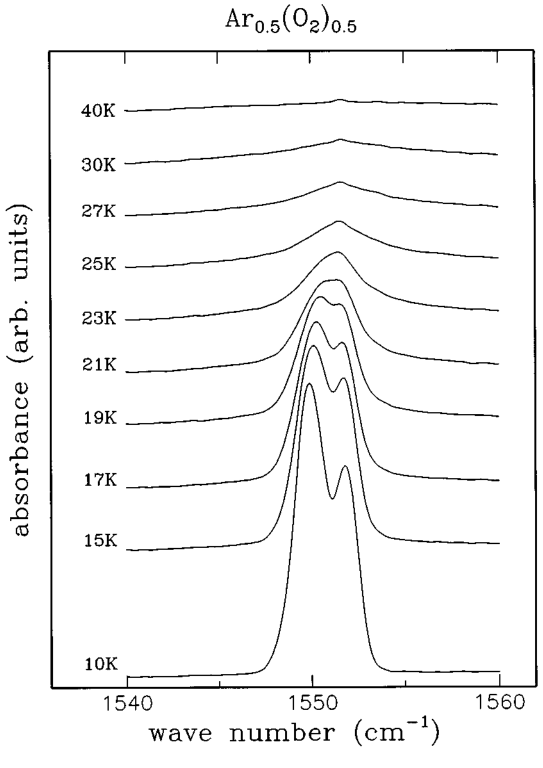

FIG. 4. The temperature dependence of the absorbance in the region of the band origin for $Ar_{0.5}(O_2)_{0.5}$.

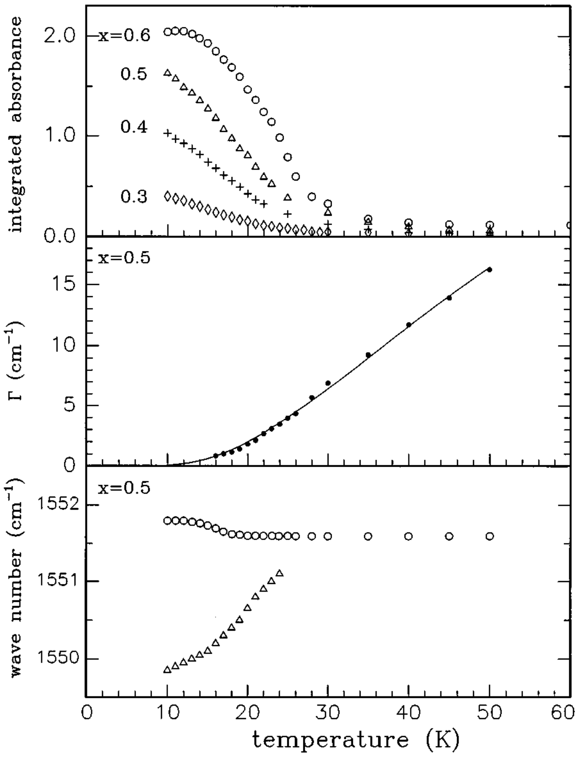

FIG. 5. The temperature dependence of the integrated absorbance between 1540 and 1560 cm^{-1} for $x=0.3$, 0.4, 0.5, 0.6 (top panel), of the width Γ half width at half maximum of the quasielastic Lorentzian component and of the vibron frequency for $x=0.5$. The solid line is a fit to an Arrhenius law $\Gamma=\Gamma_0\exp(-E/T)$ with $\Gamma_0=67$ cm^{-1} and $E=70$ K.

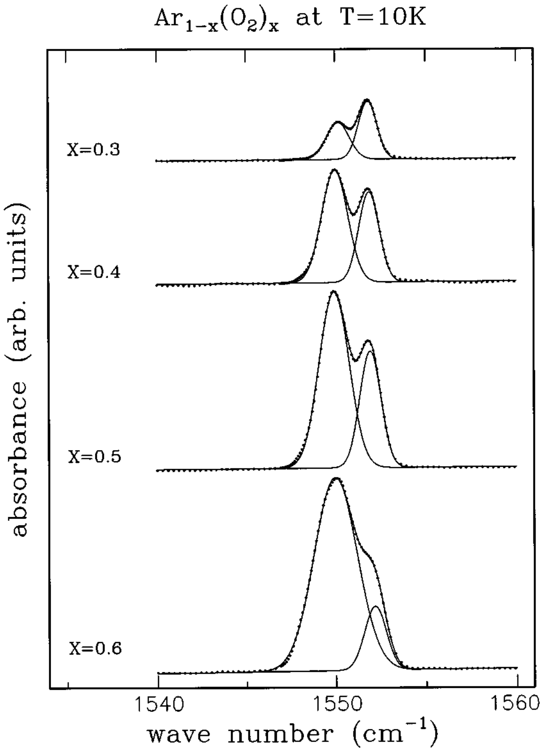

FIG. 6. The split vibron at 10 K for $x=0.3$, 0.4, 0.5, 0.6. The solid lines are the results of fits of two Gaussians to the data.

such an effect should be operating already at high T. Further below we will relate the appearance of the IR-active fundamental to the formation of the glassy state.

In the following we look at the fundamental in more detail. Figure 4 shows the evolution of the line splitting and the growth of the fundamental with temperature for $x=0.5$. Figure 5 displays the integrated absorbance above baseline in the ν interval from 1540 to 1560 cm^{-1} for $x=0.3$, 0.4, 0.5, 0.6, the splitting of the fundamental and the Lorentzian halfwidth as a function of T for $x=0.5$. As can be seen the integrated intensity of the fundamental is low at high T and increases significantly below about 25 K, while simultaneously a line splitting develops. We tried to fit line shapes to the experimental data on the fundamental. For $T<16$ K, two Gaussians, representing the split fundamental, see Fig. 6, have been fitted to the data, for $T>24$ K we used a resolution-limited Gaussian superimposed on a Lorentzian centered at the same frequency. In the intermediate T range in which the fundamental grows and splits, while simultaneously the Lorentzian wings to the fundamental become visible, any combination of trial functions appears somewhat arbitrary. We used fits with two Gaussians, either one accompanied by a Lorentzian component, the two Lorentzians having identical widths. The T dependence of the Lorentzian width is well described by an Arrhenius law, see Fig. 5. The attempt frequency is of the order of 60–70 cm^{-1} which is comparable to the average lattice frequency. The energy barrier is of the order of 70 K. Similar figures have been observed for $Ar:N_2$.[6]

Figure 6 displays the fundamental at 10 K for several x values. The total intensity increases with the oxygen content. The splitting slightly decreases from 1.8 cm^{-1} for $x=0.6$ to 1.5 cm^{-1} for $x=0.3$. The relative intensity of the higher-frequency component decreases with increasing oxygen content of the solid solutions, while its width is almost independent of the O_2 concentration. The width of the low-frequency component, however, increases with the oxygen content.

In the following we discuss possible origins for the peculiar T dependence of the frequency splitting and of the vibron intensity. Clearly this T dependence is reminiscent to a symmetry breaking connected with a phase transition. However, our complementary x-ray and neutron-diffraction measurements failed to produce any evidence such as the appearance of extra diffraction peaks or splittings of diffraction peaks for a structural or magnetic phase transition. Thus a global symmetry breaking can be ruled out. On the other hand, heat-capacity measurements for $x=0.4$,[17] and x-ray-diffraction measurements on the coefficient of thermal volume expansion for $x=0.35$ (Ref. 12) have shown that these quantities display a broad anomaly centered at about 20 K, which agrees with the temperature, where in the present experiment the O_2 fundamental splits and grows. Further information comes from measurements of the magnetic susceptibility.[18,19] According to Ref. 18, the susceptibility of the solid solutions follows a Curie-Weiss law $\chi\sim(T+\theta)^{-1}$ down to helium temperatures, the Weiss temperature θ being proportional to the O_2 concentration x, $\theta=x*60$ K. This result suggests that the magnetic interactions cannot be ignored, but obviously do not induce long-range magnetic order above helium temperature, although one may argue that the relatively high fields employed in this study, up to 1.5 T, might have been strong enough to destroy marginally stable spin structures or spin-glass patterns. Altogether we conclude that the experimental information strongly favors some type of local rather than long-range ordering in hcp $Ar:O_2$ solid solutions, $0.3<x<0.6$. We interpret this low-T state as a quadrupolar and spin-glass state.

The IR activity of the O_2 fundamental can be explained on the basis of a glassy state. The freezing into such a state, ‘‘solidification’’ in general, is due to the condensation of modes which formerly have been of the resonant or the relaxing type, namely spin-diffusive modes in the case of a spin glass and rotational modes coupled to phonons of the center-of-mass lattice in the case of quadrupolar glasses. The condensed modes of the glassy state show up as the so-called central peak in neutron and light spectroscopy measurements. In contrast to soft-mode-driven phase transitions the condensed modes cover wide regions of reciprocal space. Pertinent experimental information exists for the quadrupolar glass reference system $Ar:N_2$,[20] and in more detail for KBr:KCN.[21] Some of these modes may well be IR active. Hence the condensation will shift IR activity from the sideband to the band origin, i.e., from finite ν' values to $\nu'=0$. One may translate this view of condensed modes into a more local one, namely of distorted local environments, which then induce the IR activity of the vibron. The condensation can be either driven by random interactions or by preexisting random fields, such as stress fields introduced by alloying. The small, but nevertheless finite intensity of the vibron spike at high T may indicate that the random-field view is more appropriate.

So far it was tacitly assumed that the vibron is infinitesimally sharp and free of dispersion, thus leading to a well defined band origin. At low temperatures this is no longer true, the profile of the fundamental mirrors the frequency distribution of the vibron mode (coupled to IR-active condensed lattice modes). As discussed above the low-T vibron profile can be well described by two Gaussians, their intrinsic widths W being of the order of 0.5 to 1 cm^{-1}. This suggests that there are basically two types of inequivalent sites, either one being inhomogeneously broadened. The alternative interpretation of the band profile in terms of vibron dispersion appears less convincing. The overall width of the distribution which is of the order of 4 cm^{-1} would then correspond to the width ΔE of the vibron band $\nu(k)$. Since $\Delta E > W$, the inhomogeneous broadening should be averaged out by the propagating vibron excitation. Turning back to the former view, one wonders what type of interaction is responsible for the formation of inequivalent sites at low T.

We explore the idea that stacking faults create local hcp and fcc environments which in turn could be responsible for the splitting of the fundamental. Such stacking faults have been shown to be omnipresent in hcp $Ar:N_2$.[22] Following Prokhvatilov and Baryl'nik, hcp $Ar:O_2$ transforms into fcc around 40 K. Such a global transformation does not take place in our samples, but nevertheless an incomplete hcp-fcc transformation with a proliferation of stacking faults might be possible. However, in such a situation one would expect considerable thermal hysteresis of the vibron splitting, in contradiction to the experimental result. Hence we consider this view not convincing.

Clearly the vibron splitting is due to intermolecular interactions, of magnetic or nonmagnetic origin. For nonmagnetic interactions the hcp phase of N_2 is a useful reference. Van der Avoird, Briels, and Jansen[23] have argued that the N_2 molecules do not precess independently about the c axis, but rather do so in a correlated way, the two molecules of the hcp cell having a common inclination angle but opposite azimuthal angles, say 0° and 180°, with respect to the c axis. Such a pair configuration can give rise to a split stretching vibration with both components being IR active. For this statement we refer to the symmetry analysis by Chui, Chen, and Silvera[24] of possible high-pressure phases of solid hydrogen, one of which being the orthorhombic phase $Pmc2_1$ which is obtained by a continuation of the aforementioned configuration.

Returning to the $Ar:O_2$ system, we point out that already Prokhvatilov, Brodyanskii, and Baryl'nik[12] have argued, based on a high-T expansion of the free energy, that the anomaly of the heat capacity and of the thermal-expansion coefficient is predominantly due to magnetic, rather than to quadrupolar interactions. Indeed, these anomalies are much stronger in the magnetic system $Ar:O_2$ than in the nonmagnetic reference system $Ar:N_2$. Furthermore the relatively large values of the Weiss temperature θ support the idea that some sort of magnetic ordering should take place in hcp $Ar:O_2$ at low T. Via the molecular anisotropy term,[14] the spin direction is coupled to the orientation of the molecular axis. Thus magnetic ordering, independent of whether it is of short or long range, will affect the orientational distribution which in turn will couple to the center-of-mass lattice. In this context it is conspicuous that the c/a ratio of hcp $Ar:O_2$ deviates from the ideal value at low T.[12] The deviation follows approximately the T dependence observed for the vibron splitting and for the vibron IR intensity and is considerably larger than for $Ar:N_2$.

In any case the concept of intermolecular interactions allows us to regard the vibron splitting as measure of a local order parameter, the local ordering setting in between 20–25 K and saturating below about 15 K. In a complementary, dynamic scenario one can interpret the collapse of the splitting on heating in terms of a dephasing process of the various, here basically two, vibrational modes via low-frequency, thermally populated modes.[25,26] One may think, e.g., that the vibrational frequency of the O_2 molecule depends on its orientation with respect to the crystallographic axes. This would suggest that there are basically two inequivalent orientations at low T, perhaps one parallel to the c axis, the other one perpendicular to it. In that case the relevant low-frequency mode should be identified with a reorientation mode and the splitting would collapse in the T range in which the reorientation rate becomes comparable to the splitting.

CONCLUSIONS

The present measurements suggest that for $Ar:O_2$ mixed crystals with O_2 concentrations ranging from 0.3 to 0.6 the hcp structure is stable down to lowest temperatures. The IR absorbance of the stretching-band region of the hcp phase shows three components: (i) the density of state part is a rather smooth function of frequency. It is similar to that of the orientationally disordered γ phase of O_2; (ii) the quasielastic Lorentzian-shaped part, representing relaxing modes, in particular the O_2 reorientations. The width narrows, i.e., the relaxation rate decreases with decreasing temperature; (iii) the O_2 fundamental, which starts out as a tiny spike but grows and splits on cooling. The low-T intensity of the fundamental stems from frozen-in lattice modes coupled to the vibron. The splitting is due to a local ordering process of the molecular magnetic and quadrupolar moments. The intensity and the frequency splitting of the fundamental can be regarded as a measure of the local order parameter. We suggest that the low-T state of hcp $Ar:O_2$ solid solutions is glasslike as far as the magnetic and orientational degrees of freedom are concerned. Thus the low-T state of $Ar:O_2$ solid solutions appears to be the first example of a combined spin and quadrupolar glass state.

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