Thermal hysteresis of the dielectric susceptibility of solid oxygen in the audio frequency range

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High sensitivity measurements of the dielectric constant of solid oxygen are reported for $4<T<54$ K. The results show unexpectedly large hysteresis effects for the temperature dependence of the dielectric constant in the α and β phases of oxygen on thermal cycling below 44 K. The behavior is compared to that observed for solid N_2-Ar mixtures where the geometrical frustration of the molecular orientational ordering leads to pronounced memory effects. In contrast to solid N_2-Ar where the effects of frustration and disorder combine to form an orientational glass, there is no disorder present for pure O_2 and the hystereses are attributed to the strong frustration of the interactions.

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I. INTRODUCTION

The low-temperature structures of solid oxygen result from strongly competing magnetic and lattice effects.[1–4] Three crystalline forms are observed with well-defined transition temperatures between the different phases. The lowest temperature α phase ($T<23.8$ K at ambient pressures) is a two sublattice collinear antiferromagnet of the monoclinic lattice type $C2/m$ (Refs. 5–7) with spin alignments successively parallel and antiparallel to the b axis.[4,8–11] The molecular axes are aligned parallel to one another (ferro-orientational) along the c axis, and the magnetic moments are aligned collinearly and perpendicular to the c axis [Fig. 1(a)]. This state is the only known diatomic molecular antiferromagnet and is characterized by a magnetic Heisenberg interaction with strength $J=19.9$ K plus a smaller spin-orbit coupling. At 23.8 K the α phase transitions to a trigonal β phase with a rhombohedral $r3m$ structure[12–14] and a highly frustrated quasihelical ordering of the magnetic moments in a three sublattice structure with each dipole oriented at $2\pi/3$ with respect to its neighbor and all parallel to the $a-b$ plane [Fig. 1(b)].[15] As shown in Figs. 2(a) and 2(b), the molecular axes (electric-quadrupole moments) remain aligned along the c axis. At $T=43.8$ K the molecular alignments transition to a disordered γ phase ($Pm3m$ symmetry) with an appreciable latent heat and a large change in crystal volume. In the γ phase, both the orientation of the molecular axes and the magnetic moments are disordered.

The interesting feature of solid O_2 is that both the orientational and magnetic degrees of freedom exhibit frustration in differing degrees in the three solid phases. In the γ phase both the magnetic moments and the orientations of the molecules are disordered, and the molecular orientations are on the average disordered with respect to different axes of the lattice structure. In the β phase, the magnetic moments form a frustrated helical ordering, while the orientational moments are aligned parallel to the c axis. This parallel orientation is driven by the isotropic component of the van der Waals interactions and results in very high frustration for the anisotropic (principally quadrupolar) interactions that favor perpendicular alignments for the molecular axes. In the α phase the magnetic moments form the collinear antiferromagnetic alignment removing the frustration of the magnetic interactions, but the molecular alignments remain parallel to the c axis. The frustration of the molecular orientational interactions therefore remains largely the same at the transition from the β to the α phase.

While the general symmetry features of the three phases are well understood, the nature of the transition between the α and β phases has remained somewhat controversial. The order of the transition is still not agreed upon.[16] Stephens and Majkrzak[7] reported hysteresis for the temperature dependence of the magnetization, and Giauque and Johnston,[17] Orlova,[18] and Ancsin[19] reported evidence for a latent heat. Monte Carlo calculations using deformable cells[1] and calculations of densities for different structures[5] show abrupt changes at the $\alpha-\beta$ transition. In contrast, Fagerstroem and Hollis-Halbert[14] found no evidence for hysteresis or latent heat in measurements of the specific heat.

In order to study this system more deeply we have carried out high-precision measurements of the dielectric constant, ε. The dielectric susceptibility[20,21] has been shown to be a very sensitive probe of the local ordering of molecular orientations in simple diatomic molecular solids such as N_2 where the ordering is driven by local electrostatic interac-

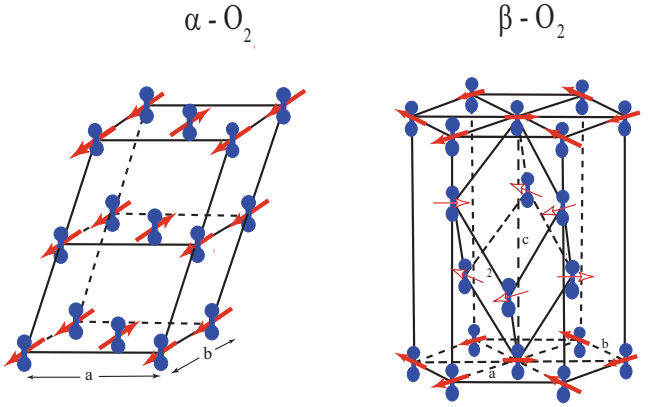

FIG. 1. (Color) Schematic representations of the structure of the α and β phases of solid oxygen, showing the ordering of the orientational axes (blue dumbells) along the c axis and the ordering of the magnetic moments in the $a-b$ plane (red arrows).

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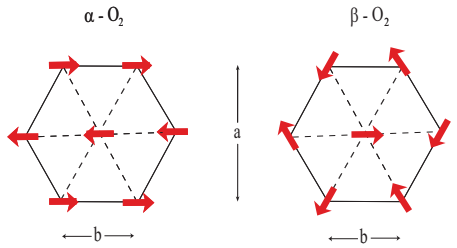

FIG. 2. (Color) Top view of the ordering of the magnetic moments in the $a-b$ plane of the α and β phases of solid O_2. The molecular axes are aligned normal to this plane.

tions that are highly frustrated. It is important to note that the dielectric measurements give the generalized susceptibility for applied electric fields that perturb the molecular axis alignments and in the absence of anisotropic magnetoelastic interactions would not be sensitive to the magnetic degrees of freedom. Measurements of the temperature dependence $\varepsilon(T)$ have been used to follow memory effects and hysteresis in the development of local orientational ordering in molecular solids such as solid N_2, solid N_2-Ar mixtures, and solid CO. These latter solids exhibit strong geometrical frustration because of the topological impossibility of realizing the minimum energy for all pairs of neighboring quadrupolar molecules, and in the presence of small amounts of disorder lead to orientational or quadrupolar glass states.[22] Striking phenomena including strong hysteresis and field cooling memory effects have been observed for these systems.[21] Given the high degree of frustration of both the orientational and magnetic interactions in solid oxygen, similar hysteresis effects could be anticipated for solid O_2.

To first order the frustration of the orientational interactions does not change at the $\alpha-\beta$ phase transition and the hysteresis effects would be expected to persist for measurement of the electric-field response when traversing the $\alpha-\beta$ phase boundary. The interest in comparing the observations of thermal cycling in the frustrated phase of solid O_2 with the behavior observed for solid N_2-Ar mixtures is that for the latter, the presence of disorder played an important role and was shown to determine the "glass-transition" temperatures and the magnitude of the memory effect or hysteresis on thermal cycling. The question we sought to answer in the studies reported here was whether the presence of disorder is essential for the observation of hysteresis on thermal cycling in the phases exhibiting frustration for the anisotropic electrostatic interactions.

II. CORRELATIONS AND MEMORY EFFECTS

Dielectric spectroscopy can be used as a high sensitivity method to determine the molecular reorientation rates and local ordering in polar and nonpolar systems. The local orientational ordering of molecular axes is specified by two sets of parameters: (i) the local orthonormal axes (x_i, y_i, z_i) associated with the mean orientation of the internuclear axis of each molecule i and (ii) the intrinsic quadrupolar parameters given by the mean (time-averaged) alignment $\sigma_i = \langle 2z_i^2 - (x_i^2 + y_i^2)\rangle$ and the mean eccentricity $\eta_i = \langle x_i^2 - y_i^2\rangle$ of the molecules with respect to these local axes. In terms of the polar angles (θ_i, ϕ_i) that specify the instantaneous alignment of the molecule with respect to these mean axes, $\sigma_i = \langle (3\cos^2\theta_i - 1)/2\rangle$ and $\eta_i = \langle 2\sin^2\theta_i \cos 2\phi_i\rangle$. The short-range correlations between the axes and the order parameters distinguish local ordering from independent-particle paraelectric behavior.

The anisotropic component of the dielectric susceptibility of an ensemble of nonpolar molecules is directly related to the local order parameters. The polarizability α is separable into an isotropic component $\alpha_{\rm iso}$ and an anisotropic component $\alpha_{\rm aniso}$. The average polarizability is defined as $\alpha_0 = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$, where $\alpha_\parallel$ and $\alpha_\perp$ are the polarizabilities parallel and perpendicular to the molecular axes, respectively. The isotropic component is simply $\alpha_\perp$ and the anisotropic component is given by[23–25]

$$\alpha_{\rm aniso} = \frac{1}{3}\Delta\alpha\langle\langle 3\cos^2\theta_E(i) - 1\rangle\rangle, \tag{1}$$

where $\Delta\alpha = (\alpha_\parallel - \alpha_\perp)$. $\theta_E(i)$ is the polar angle specifying the orientation of the applied electric field with respect to the instantaneous molecular axes (x_i, y_i, z_i) of the ith molecule. The average $\langle\langle\cdots\rangle\rangle$ refers to both a configurational and a time average. The anisotropy is very high for O_2 molecules, $\Delta\alpha/\alpha_0 = 0.72$,[26] and as a consequence, dielectric measurements can provide a powerful tool for probing local molecular ordering over a range of frequencies that are especially relevant to the dynamical time scale of the intermolecular correlations in solid O_2 and as was shown for solid N_2-Ar mixtures.[21]

The polarizability is determined from the observed dielectric constant ε using the Clausius-Mossotti relation $\alpha = \frac{3}{4\pi N}(\varepsilon - 1)/(\varepsilon - 2)$. $\alpha_{\rm aniso}$ depends directly on the local order parameters, the alignment $\sigma_i(T)$, and the eccentricity $\eta_i(T)$ through the relation

$$\alpha_{\rm aniso} = -\frac{1}{3}\Delta\alpha\left\{\sigma_i(T)P_2[\cos\Theta_E(i)] + \frac{3}{2}\eta_i\sin^2\Theta_E(i)\cos[2\Phi_E(i)]\right\}. \tag{2}$$

$[\Theta_E(i), \Phi_E(i)]$ are the polar angles specifying the orientation of the electric field with respect to the local symmetry axes. $\alpha_{\rm aniso} = 0$ at high temperatures, but at low temperatures there is a finite contribution depending on the nature of the ordering and the correlations between the order parameters and the local molecular axes. If there are no correlations, the variables (σ_i, η_i) and $[\Theta_E(i), \Phi_E(i)]$ are separable, and one can perform independent averages over the positions and the order parameters. For a powder sample, the average vanishes if the variables are separable. This result is very important for the current experiments because the background signal vanishes for the disordered phase and for simple periodic ordering. The measurements are therefore particularly sensitive to the correlations between the order parameters and the configurations of the molecular axes. It is important to note that for the trivial low-temperature paradielectric state with molecular axes and order parameters locally frozen, these

correlations simply vanish. The correlations provide the key to probing the underlying nature of systems that show glassy behavior and aging effects.

III. EXPERIMENTAL MEASUREMENTS

In the experiments reported here, the applied electric fields are used to measure the dielectric susceptibilities and their thermal history in order to determine the dynamical behavior of the molecular alignments. The external electric field by itself is not used as a means of generating glass behavior, as it is not the field conjugate to the order parameter. Indirectly however, because of the coupling between the centers of mass and the orientation of the molecules arising from steric hindrance, there will be a secondary effect where applied electric fields will induce reorientations that can lead to measurable effects in high sensitivity measurements.

Measurements of the dielectric constant $\varepsilon(T)$ were carried out using a three terminal ac capacitance bridge having sensitivities of 2×10^{-9} in the real part of the dielectric constant and 2×10^{-7} in the dielectric loss.[27] The bridge consists of two low-temperature coaxial capacitors carefully matched so that spurious temperature variations and losses cancel to first order over the entire temperature range investigated. No hysteresis or field-dependent responses were observed to an accuracy of 10^{-5} with both cells empty.

The samples were prepared from ultrahigh-purity O_2 gas (99.999%) and condensed as a liquid using a fine capillary that was equipped with a heater to prevent condensation in the fill line. After condensation the samples were cooled to the solid-liquid transition at 54 K and annealed for 8 h. During annealing, the saturated vapor pressure was monitored to check for further gas flow in order to reduce possible voids as much as possible. The absolute value of the dielectric constant measured at 4.2 K from several solid samples showed that additional gas did not enter the sample cell. The temperatures were measured using a calibrated germanium resistance thermometer[28] located in a well in the outer casing of the low-temperature capacitance cell.

Figure 3 shows the observed variation of the dielectric constant for an excitation field of 5 kV/m at 1 kHz. The sample was first cooled slowly (over 4 h) to 4.2 K with no electric field present. The field was then turned on and the values of ε measured as a function of temperature while warming were shown by the red open squares. The time interval between each data point was 10 min. The warming sequence was halted at 37.6 K for the first set of measurements in order to remain in the β phase and well below the $\beta-\gamma$ transition in order to exclude pretransitional effects. The characteristic lambda-shaped variation (drop) in ε was observed to be invariant to within 0.07 K of the thermal cycling. The actual temperature of the transition given by the calibrated thermometer was 2.9% lower than the accepted value of the $\alpha-\beta$ transition in the literature. This fractional deviation was also seen for the $\beta-\gamma$ transition. We therefore adopted the position of Szmryka-Grzebyk *et al.*[16] that the two phase transitions should be taken as fixed points at 23.867 and 43.796 K, respectively, for the $\alpha-\beta$ and $\beta-\gamma$ transitions and used these fixed points to recalibrate the thermometer reading. All the temperatures given in the figures correspond to this recalibration.

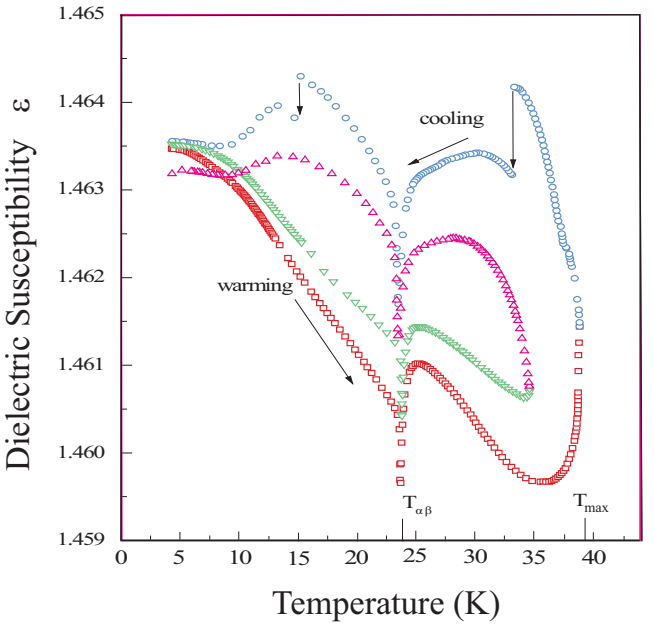

FIG. 3. (Color) Temperature dependence of the ac susceptibility, $\varepsilon(T)$, of solid O_2 for two temperature cycles in the α and β phases. The sample was first cooled in the absence of an electric field to 4.2 K, and ε was then measured at 1 kHz for a field strength of 5 kV/m on warming (red squares) to 37.6 K, subsequent cooling (blue circles) to 4.2 K, and the cycle repeated, [green triangles (warming) and magenta triangles (cooling)] for $T_{max}=33.5$ K.

The results for ε on cooling (with no significant holding time at 37.6 K and with the ac field held at the same value) are shown by the open blue circles. We observe two unexpected features: (i) there is strong hysteresis in the absolute value of $\varepsilon(T)$ for pure O_2 but the characteristic λ-shaped drop at the phase transition is invariant with cooling cycle and (ii) sharp drops are seen for ε on cooling, which were not seen on warming. On subsequent warming, with no holding time at 4.2 K, the values of ε are shown by the green down triangles of Fig. 3, with absolute values larger than observed on the first warming cycle, but with the same amplitude and shape (within the accuracy of the base line estimation) for the $\lambda(T_{\alpha\beta})$ transition. In this sequence, the warming was halted at 33.5 K to determine if the hysteresis depended on the final upper temperature of the cycle. On cooling below 33.5 K (shown by the magenta up triangles), strong hysteresis is again observed but considerably reduced compared to the first cycle.

The hysteresis was studied for a second sample for temperature excursions to 47 K, well above the $\alpha-\beta$ and $\beta-\gamma$ phase transitions, but appreciably below the melting point (54 K). As described above for the first sample, the second sample was carefully annealed at the melting point and cooled to 4.2 K with no applied ac electric field. The fractional deviation $\delta\varepsilon/\varepsilon$ from the value measured at 4.2 K is shown in Fig. 4. The data obtained during the first warming cycle are shown as red squares and the subsequent cooling from 47 to 4.2 K as blue circles. The next warming cycle, shown by triangles (green), exhibits an appreciable differ-

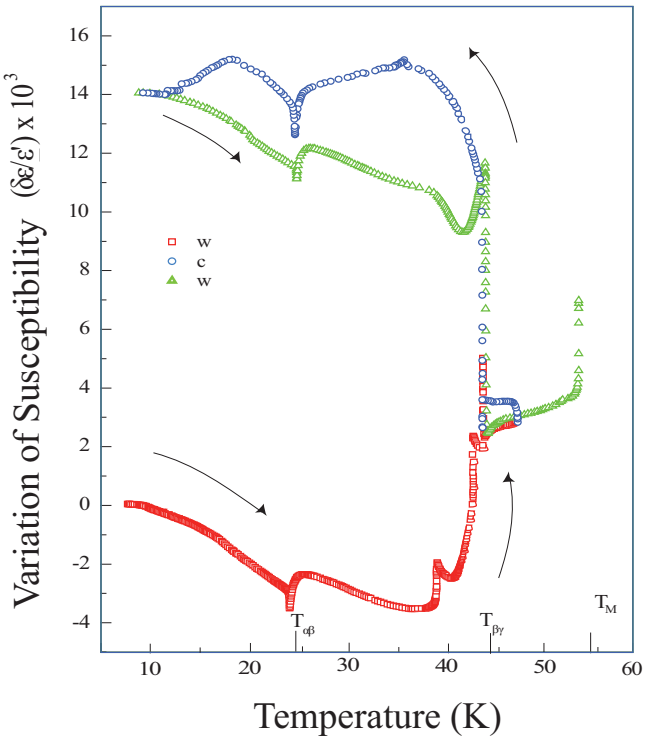

FIG. 4. (Color) Temperature dependence of the variation $\delta\varepsilon(T)$ of the observed ac susceptibility for solid O_2 for temperature cycles extending into the disordered γ phase. The sample was first cooled in the absence of an electric field to 4.2 K, and then ε measured at 1 kHz for a field strength of 5 kV/m on warming (red squares) to 47 K, subsequently cooled (open blue circles) to 4.2 K, and the cycle repeated (green open triangles).

ence in the absolute values of ε in the α and β phases, but close to the values previously measured in the disordered γ phase. Each complete thermal cycle took 3 h. As for the first sample, the shape and the magnitude of the λ feature at the $\alpha-\beta$ transition appear to be invariant with respect to the thermal cycles. The $\beta-\gamma$ transitions are marked by sharp changes in ε that are quite reproducible in magnitude but preceded on the low-temperature side by history dependent variations. The area of the closed hysteresis loop for the cycle restricted to the $\alpha-\beta$ phases is quantitatively consistent with those in Fig. 3.

IV. DISCUSSION

The pronounced hysteresis on thermal cycling with surprisingly large variations in $\varepsilon(T)$, of the order of 0.3% throughout the β and α phases, is similar to the variation observed for solid N_2 and N_2-Ar solid mixtures.[21] In the latter studies, the variations were attributed to field-induced changes in a complex free-energy landscape of the frustrated electric-quadrupole interaction energies in the quadrupole glass region of the phase diagram. The case of solid O_2 is different. We consider the frustration of the orientational interactions separate from that of the magnetic interactions to the lowest-order approximation. The magnetic interactions are highly frustrated in the β phase and this is only partly relieved in the collinear antiferromagnetic α phase. For the orientational degrees of freedom, however, the frustration is invariant at the $\alpha-\beta$ phase boundary except for the fluctuations induced by the relatively strong magnetoelastic interactions[2,5] at the phase transition. These fluctuations result in the sharp dip in ε at the transition which is observed to be the same to a good approximation for all thermal cycles. The constancy of the average molecular alignments and at the $\alpha-\beta$ transition explains why we see no significant change in the hysteresis behavior once we factor out the fluctuation dip at the transition itself. There is, however, a strong coupling of the magnetic and elastic interactions, and as a consequence, a weak coupling of field-induced effects on the anisotropic component of the magnetoelastic interactions would be present. The effects observed for O_2 therefore appear to be related to nonequilibrium effects for samples aged in the β phase where applied electric fields are indirectly coupled to the anisotropic magnetoelastic interactions.

It is significant to note that the "sudden" drops in ε were only observed on cooling (as was observed for solid N_2 but in a very different temperature-field range). The lack of such events on warming while consistent with an erasure of memory effects with aging is expected to occur as a result of the release of the irreversible stress at random pinned sites. In solid oxygen this stress is generated by the very large magnetoelastic and orientational-elastic interactions, for example, the lattice expands discontinuously by 5% at the $\alpha-\beta$ phase transition. This conjecture for the origin of the sharp jumps in ε is supported by the fact that the number and the amplitude of the sharp dips are reduced considerably on repeated thermal cycling. This interpretation is also consistent with the observation that the sharp changes in ε were not significant for small thermal cycles restricted to the α phase. Furthermore, as shown in Fig. 5, the hystereses do not affect the distinctive variation at the $\alpha-\beta$ transitions despite the wide variation in the areas of the hystereses with different thermal cycles. Although the shape and the depth of the change in ε at the transition appear to be closely the same for different cycles, we did observe a small hysteresis with the transition occurring at 0.3 K higher on warming than on cooling for two different cycles. This suggests that the $\alpha-\beta$ transition is almost completely dominated by the magnetic interactions and supports the claim that the observed dependences on thermal history are due to field effects associated with the orientational degrees of freedom on cycling and aging and not spurious thermomechanical effects.

For the N_2-Ar quadrupolar glass states, the observed dependence of the areas of the hystereses on the temperature excursion was compared to the predictions of the generalized fluctuation-dissipation models of Cugliandolo and Kurchan[29] and Parisi.[30] In these models the off-equilibrium response function $\mathcal{R}(t,t_w)$ at time t, following a waiting period t_w, obeys $\mathcal{R}(t,t_w)=\beta\int\chi(\mathcal{C})d\mathcal{C}$, where χ is a generalized susceptibility and $\mathcal{C}$ refers to a normalized order-parameter correlation function. For equilibrium states, $\chi(\mathcal{C})=1$ and $\mathcal{R}_{\mathrm{eqm}}=\beta Dt$, where the familiar fluctuation-dissipation theorem with $\beta=1/k_BT$ and D as the diffusion constant. In the glassy states following aging, Cugliandolo and Kurchan[29] showed that for simple replica symmetry breaking, $\chi\sim T/T_{\mathrm{dyn}}$, where T_{dyn} gives the characteristic energy scale for glassy dynam-

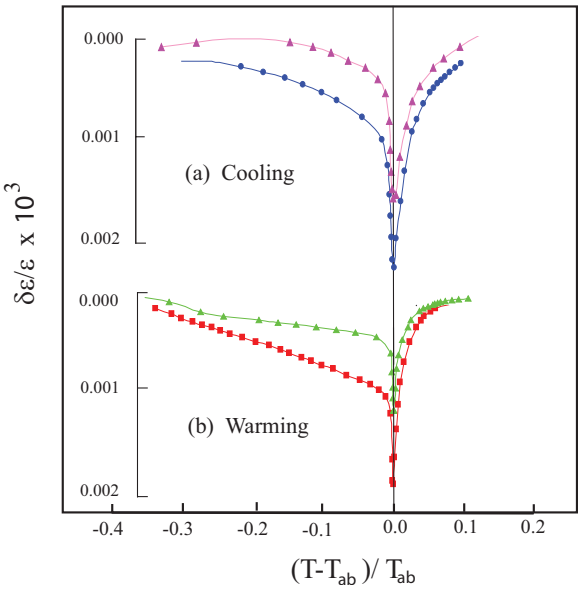

FIG. 5. (Color) Temperature variation of the normalized change in the ac susceptibility, $\delta\varepsilon(T)/\varepsilon$, of solid O_2 in the vicinity of the $\alpha-\beta$ phase transition for (a) cooling and (b) warming for the two thermal cycles shown in Fig. 3. A baseline has been removed from the data shown in Fig. 3, and each curve is separated vertically for clarity. The depth of $\varepsilon(T)$ is consistent on warming and on cooling, but the temperature dependence on warming is sharper than that observed on cooling.

ics. For the current studies, we therefore compare the area of the hystereses $\mathcal{A}=\Sigma k_B T(\delta\varepsilon/\varepsilon)$ with the temperature excursion $\delta T=T-T_{\alpha\beta}$. The variation of $\mathcal{A}/\mathcal{A}_{\max}$ as a function of δT is shown in Fig. 6 for $\mathcal{A}_{\max}=6.0\times10^{-1}$. The solid line shows the variation $\mathcal{A}/\mathcal{A}_{\max}=(\delta T/T_{\rm dyn})^2$ for $T_{\rm dyn}=67$ K. The value of 67 K for $T_{\rm dyn}$ is to be compared with the calculated mean-field magnetic energy $\langle H_M\rangle=76$ K by Etters *et al.*[3] and the effective total exchange energy $z|J|=64$ K by DeFotis.[4]

While the solid O_2 samples studied here have no substitutional disorder compared to that created deliberately for the N_2-Ar solid mixtures, the samples of solid O_2 are not expected to be totally free from the presence of disorder. The elastic stresses in this system induced on thermal cycling because of the strong orientational-elastic and magnetoelastic interactions can lead to disorder effects even in the absence of substitutional disorder. The stress sites are expected to be distributed randomly and could even be sufficient to have the same effect as the imposed substituional disorder in N_2-Ar systems.

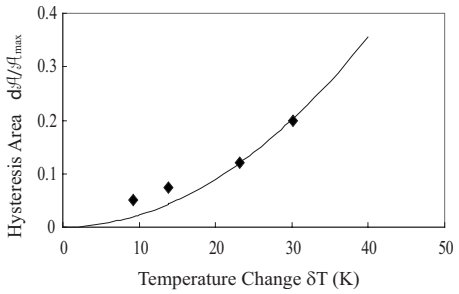

FIG. 6. Temperature variation of the normalized areas $\mathcal{A}(T)$ of the hystereses observed in the ac dielectric susceptibility $\varepsilon(T)$ of solid O_2. The data points are from Table I. The solid line is given by $\delta\mathcal{A}/\mathcal{A}_{\max}=(\delta T_{\alpha\beta}/T_{\rm dyn})^2$ with $T_{\rm dyn}=67$ K.

V. CONCLUSION

Although there is a clear understanding of the structure of the two magnetic phases of solid oxygen, the detailed dynamics and approach to equilibrium, particularly in the magnetically frustrated β phase where both the magnetic and orientational interactions are highly frustrated, have not been studied in any detail. Measurements of the dielectric response show strong memory effects for thermal cycles in the frustrated β phase, and the quantitative value of the hysteresis scales with the amplitude of the excursion into the β phase. These memory effects are common to other glass formers. The special interest in these results is that the simple molecular solids provide a window for probing glass formation in one of the most straightforward examples of frustration and the effects of disorder on frustration. Furthermore, for these systems the experimenter has access to the relevant time scales for the glass state: milliseconds to hours for the molecular systems, as opposed to years or longer for the common silicate glasses.

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