Emergence of novel phase of solid oxygen in ultrahigh magnetic field

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Abstract. Faraday discovered the magnetism of molecular oxygen in 1850, and since then, oxygen has attracted significant interests as a ubiquitous but exotic molecular magnet. In solid oxygen, the magnetic energy through the exchange interaction is comparable to the van der Waals cohesive energy, resulting in a strong spin-lattice correlation. We reported the discovery of a magnetic-field-induced phase transition of solid oxygen using ultrahigh magnetic fields up to 186 T. This is the first experiments demonstrating the phase control through the spin by applying a magnetic field. Magneto-optical absorption measurements of the α phase at low temperatures revealed that visible light absorption suddenly ceases and the background transparency dramatically improves above the critical field. The large hysteresis in these data indicates a first-order transition with a relaxation time on the order of microseconds. The results strongly suggest the reconstruction of the O₂ molecular geometry by the magnetic field, which causes that the antiferromagnetic phase collapses and the field-induced phase should have an isotropic crystal structure. Since all of the known phases of O₂ are induced in high pressure, the discovery of a field-induced phase is noteworthy in the long history of solid O₂ studies.

1. Introduction

In molecular solids, the electric intermolecular interaction generally determines the alignment of molecules and the resultant crystal structure. The van der Waals force forms a closed packed structure in noble gas elements, and the electrostatic quadrupolar interaction is also important in diatomic molecules such as N₂ and also in CO₂ [1].

In contrast to these molecules, molecular oxygen O₂ has a magnetic moment with the spin quantum number  S = 1. The exchange interaction, which depends on the alignment of molecules, strongly affects the binding energy. For each spin state of an O₂–O₂ pair (total spin of  S₁ = 0 or 2), the intermolecular potential as a function of the O₂ orientation and intermolecular distance can be obtained from ab initio calculations of the electrostatic and exchange contributions to the binding energy [2]. The spin-dependent intermolecular potential indicates that the energy of an O₂–O₂ pair is the lowest in the rectangular parallel H geometry with the singlet spin state  S₁ = 0 (an intermolecular distance of  3.23 Å) and that the lowest energy for the quintet state  S₁ = 2 is in a crossed X geometry. For solid O₂, the molecular orientation and intermolecular distance are close to those of the H geometry, which is stable for the singlet state.
In solid oxygen $\gamma$ phase (54.4–43.8 K), orientationally disordered molecules form an A15-type cubic structure [3]. Disk-like rotating sites on the cubic face show antiferromagnetic correlation mainly through the H geometry coupling. The $\gamma$–$\beta$ transition occurs at 43.8 K due to the ordering of the molecular axis [3]. As a result, the crystal transforms to the rhombohedral structure with the basic arrangement of the H geometry. Geometrical frustration in the triangular lattice of the $\beta$ phase suppresses the antiferromagnetic long-range ordering, but ordering takes place at the $\beta$–$\alpha$ transition at 23.9 K [3]. The deformation of the triangular lattice, while retaining the H geometry molecular coupling, releases the antiferromagnetic frustration. Even under high-pressure conditions, the H geometry is robust in the $\delta$ and $\epsilon$ phases [4–7], which are stable under pressures of 6–8 and 8–96 GPa, respectively. However, the H geometry should not be stable in a strong magnetic field in which the magnetization is saturated.

Ten years ago, the O$_2$–O$_2$ dimer was successfully synthesized by using nanoporous coordination polymers [8]. X-ray diffraction measurements at low temperatures revealed that the H geometry, as in the solid O$_2$, is robust in the dimer system. However, the magnetization process with a metamagnetic-like behavior could not be interpreted with $S = 1$ Heisenberg antiferromagnetic dimer model. To explain the experimental results, they invoked a scenario in which there are excited states of other geometries, e.g., the S or X type [9, 10]. This scenario indicates that a molecular rearrangement may occur in a magnetic field. It was also found that the thermally excited states lead to deviations from the H geometry at higher temperatures. These combined results, obtained on dimers, led to the prediction of a field-induced structural phase transition in solid O$_2$.

Recently we reported the discovery of a novel phase of solid O$_2$ that can be demonstrated by the magnetization measurements and magneto-optical spectroscopy in an extraordinarily strong magnetic field [11]. The experiments indicate this is the result of a first-order transition that is both a magnetic and structural transition: the antiferromagnetic phase collapses and the crystal symmetry changes. In this paper, the results of magneto-optical spectroscopy are mainly discussed.

2. Experimental

A single-turn coil technique was used to generate pulsed magnetic fields [12]. The field was pulsed for approximately 8 µs in a destructive manner. Polycrystalline $\alpha$ oxygen was grown with cooling in a $^4$He-flow-type cryostat made of Bakelite [13]. In the sample cell of the cryostat, the internal gas was substituted with high-purity oxygen (99.999%). A high-speed streak camera with a polychromator was used for the magneto-optical spectroscopy. The time dependence of the transmitted light intensity through the solid oxygen was measured using a Xe arc flash lamp as the light source. Optical fibers were used for the delivery and collection of light. The temperature was monitored with a RuO$_2$ thermometer, which was buried in the sample space. The details of the experimental procedure are shown in the supplement materials in the previous paper [11].

3. Results and Discussion

Figure 1a shows the magnetic field waveform used for the magneto-absorption spectroscopy of solid oxygen in the $\alpha$ phase; absorption spectra at 21.6 K, measured continuously as a function of time, are shown in Fig. 1b. The absorption strength is represented by the optical density ($\text{O.D.} = -\log_{10}(I/I_0)$) on a color scale, where $I$ and $I_0$ are the intensities of the transmitted light through the sample cell with and without oxygen, respectively. Figure 1c shows the absorption spectra obtained by taking the cross section of the results in Fig. 1b at different magnetic field strengths. The spectra are vertically shifted for better visualization. The absorption band observed at around 2.14–2.20 eV is due to the bimolecular transition of O$_2$ [14-17] and defined as the R-band in this paper (this absorption band is responsible for the light blue color of liquid and solid oxygen). As the field increases, the absorption peak intensity decreases accompanied by a considerable broadening, before the peak disappears at around 150 T. The broadening of the absorption peak is understood as a result of the orbital Zeeman effect in the excited state ($\Delta \Lambda \Delta$) [14, 15]. With the disappearance of the peak, the transmission abruptly doubles in magnitude (Fig. 1b). At higher fields, the absorption peak is completely absent...
within the limits of the present experimental accuracy. When the field is decreased, the absorption peak reappears at around 70 T, and simultaneously, the oxygen becomes opaque, reverting to the initial condition before the magnetic field is applied. The observed large hysteresis strongly indicates the first-order transition. Therefore, the drastic changes of the optical properties are suggested to be due to the structural phase transition.

The magnetic field dependence of the absorption intensity of the R-band is shown in Fig. 2, where the intensity $A(H)$ is normalized by that at zero field $A(0)$. In the bimolecular optical absorption process, two oxygen molecules need to simultaneously transit from magnetic initial states ($^3\Sigma_g^+$) to nonmagnetic excited states ($^1\Delta_g$) via one-photon absorption, where $^3\Sigma$ and $^1\Delta$ represent the electronic states of an O$_2$ molecule of $S = 1$ and 0, respectively. Only antiferromagnetic pairs ($S_T = 0$) of initial states participate in the optical transition, as spin must be conserved in the dipole transition. Therefore, the disappearance of the R-band at 150–170 T strongly indicates the disappearance of singlet pairs, i.e.
the saturation of the magnetization [18]. The abrupt change in the absorption intensity, indicated by the arrows in Fig. 2, suggests the presence of a metamagnetic transition to the saturated magnetization state. The first-order metamagnetic transition has also been confirmed in the magnetization measurement [11].

The large increase of the transmission at 150–170 T over the whole photon energy range (Fig. 1b) cannot be explained in terms of electronic optical transitions that occur only in a specific photon energy range. It is proposed, therefore, that classical light scattering from the domain boundaries inherent to polycrystalline α oxygen is significantly reduced in this region due to the field-induced phase transition. In general, polycrystalline domains are formed during the γ–β phase transition with decreasing temperature due to the large volume contraction and the symmetry reduction from the cubic (γ) to rhombohedral (β) structure [3]. Since the crystal symmetry is lowered further to monoclinic in the α phase, it is almost impossible to obtain a single crystal of α oxygen. The α and β phases are thus optically opaque, similar to frosted glass, because of the strong light scattering from the domain boundaries with an anisotropic refractive index. The significant decrease in the light scattering is thus understood to result from the change in the crystal structure. When the crystal symmetry is isotropic, e.g. cubic, the matching conditions between the refractive indices of the domains would be improved. Moreover, domains with isotropic symmetry may form larger domains, and hence light scattering from the domain boundaries almost disappears in the high-field phase.

Figure 3 shows the field dependence of the transparency at 2.10 eV for fields with different maximum field strengths; each field has a different sweep speed, as shown by the waveforms in Fig. 3b. Around this photon energy, absorption due to the R-band is negligible and the optical transmission reflects the degree of classical light scattering. The normalized scattering S(H) is defined here as

$$S(H) = \frac{\log_{10}(I_0/I)}{[\log_{10}(I_0/I)]_{H=0} - [\log_{10}(I_0/I)]_{\min}},$$

where \(\log_{10}(I_0/I)\) has the same definition as the optical density but in this case represents the degree of light scattering, \(\log_{10}(I_0/I)\) \(_{H=0}\) is the initial value at 0 T, and \(\log_{10}(I_0/I)\) \(_{\min}\) is the minimum value for each field strength. The scattering S(H) is nearly constant for a magnetic field of 117 T (green curve), while there is an abrupt decrease in S(H) for a field of 128 T (yellow curve). The critical field is thus

![Figure 3](image-url)
between 117 and 128 T for this time scale of the field sweep. The dependence on the sweep speed implies the transition has a long relaxation time on the microsecond scale, which supports the structural phase transition.

After applying the magnetic field, light scattering from the domain boundaries in the solid oxygen changes as shown in Fig. 3a, and Fig. 2 also showed that $A(H)/A(0)$ takes a value larger than the value before applying magnetic field, indicating different optical paths in the oxygen crystal. Thus, rearrangement of different-sized domains before and after the appearance of the high-field phase is likely to occur.

Both the metamagnetism and the structural phase transition can be explained consistently by a cooperative phase transition involving a change in the exchange interaction and a geometrical rearrangement of the oxygen molecules. Since the exchange interaction dominates the molecular arrangement in solid O$_2$ as described above, it is plausible that the O$_2$–O$_2$ couplings change from the antiferromagnetic H geometry to another geometry with the weak antiferromagnetic interaction or the ferromagnetic interaction. This molecular rearrangement produces an isotropic crystal structure with the saturated magnetization.

Determining the crystal structure of the high-field phase is an intriguing and important task. Standard methods such as X-ray and neutron diffraction are almost technically impossible to perform in magnetic fields of over 100 T, and so a technical breakthrough will be required to experimentally clarify the crystal structure. At present, we speculate that one possible crystal structure is a modified dry ice structure (cubic phase of solid CO$_2$ at atmospheric pressure), which is a stable arrangement with respect to the quadrupolar interaction. The solid N$_2$ α-phase and D$_2$ α-phase both have the dry ice structure [1]. The quadrupole moment of $-0.4 \times 10^{-26}$ esu in O$_2$ is smaller than that of N$_2$ ($-1.4 \times 10^{-26}$ esu) and CO$_2$ ($-4.3 \times 10^{-26}$ esu) but is comparable to that for D$_2$ ($0.64 \times 10^{-26}$ esu) [1]. Ab initio calculations of the exchange interaction in this arrangement are essential for further discussion of the crystal structure in the high-field phase.

4. Summary

We found the magnetic-field-induced phase transition of solid oxygen using ultrahigh magnetic fields up to 186 T. The magneto-optical measurements of the α phase revealed that the absorption intensity of the R-band suddenly ceases and the background transparency dramatically improves above the critical field. The disappearance of the R-band strongly indicates the saturation of the magnetization. The significant decrease in the light scattering is understood to result from the change in the crystal structure. These results strongly suggest the reconstruction of the O$_2$ molecular geometry by the magnetic field, which causes that the antiferromagnetic phase collapses and the field-induced phase should have an isotropic crystal structure.

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