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Novel Phase of Solid Oxygen Induced by Ultrahigh Magnetic Fields

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Magnetization measurements and magnetotransmission spectroscopy of the solid oxygen α phase were performed in ultrahigh magnetic fields of up to 193 T. An abrupt increase in magnetization with large hysteresis was observed when pulsed magnetic fields greater than 120 T were applied. Moreover, the transmission of light significantly increased in the visible range. These experimental findings indicate that a first-order phase transition occurs in solid oxygen in ultrahigh magnetic fields, and that it is not just a magnetic transition. Considering the molecular rearrangement mechanism found in the O_2-O_2 dimer system, we conclude that the observed field-induced transition is caused by the antiferromagnetic phase collapsing and a change in the crystal structure.

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Since Faraday discovered that molecular oxygen is paramagnetic in 1850, oxygen has attracted significant interest as a ubiquitous but exotic molecular magnet [1]. The paramagnetism of gaseous oxygen arises from the spin quantum number $S = 1$ of O_2. In condensed oxygen, the exchange interaction between O_2 molecules develops and contributes to the cohesive energy in addition to the van der Waals force. Particularly in solid oxygen, the magnetic contribution to the condensation energy is non-negligible and affects the resultant crystal structure through spin-lattice coupling.

At atmospheric pressure, solid oxygen has three phases with different magnetic and crystal structures [2]. High-temperature γ oxygen (54.4–43.8 K) is a paramagnetic phase where orientationally disordered molecules form an A15 cubic structure. The γ-β transition occurs at 43.8 K because of the ordering of the molecular axis parallel to the c axis, and the short-range antiferromagnetic (AFM) correlation develops. At the transition, the crystal symmetry changes from cubic to rhombohedral, accompanied by a large volume contraction. As the temperature is reduced further, the β-α transition occurs at 23.9 K, because of long range AFM ordering where the crystal transforms from rhombohedral to monoclinic. Because of the strong spin-lattice coupling, solid oxygen is regarded as a spin-controlled crystal [3].

Since magnetic energy affects the packing structure of solid oxygen, external magnetic fields may alter the crystal structure through magnetization. Previously, magnetization measurements of the solid oxygen α phase have been performed up to 50 T [4]. However, at these field strengths, the magnetization curve is almost linear and no phase transition is observed. Subsequently, no higher field experiments were performed on solid oxygen because of technical difficulties of conducting experiments in ultrahigh magnetic fields. Therefore, little is known about the effect of magnetic fields on the phase diagram of solid oxygen.

From a theoretical point of view, the effect of magnetic fields on solid oxygen is intriguing. *Ab initio* calculations of an O_2-O_2 dimer predict the spatial rearrangement of the O_2 molecules depending on the magnetization [5–7]. The two O_2 molecules normally couple in a parallel alignment, called H geometry, where the AFM exchange interaction in the O_2-O_2 dimer is large and the singlet state ($S_T = 0$, S_T is the total spin) is favored. However, when the dimer is magnetized ($S_T = 2$), other molecular arrangements such as S geometry (canted) or X geometry (crossed) should be induced (Fig. 1) [6,7]. This is because the exchange interaction in the O_2-O_2 dimer becomes ferromagnetic (FM) for S or X geometries as a result of the way of overlapping of the molecular orbitals [5]. Therefore, in very high magnetic fields, the FM S or X geometry should be induced instead of the AFM H geometry. Experimental results supporting these calculations have been reported in
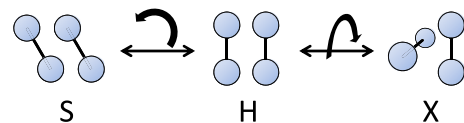

FIG. 1 (color online). Schematic of the geometrical rearrangement for the O_2-O_2 dimer, from H geometry (parallel) to S geometry (canted) or X geometry (crossed). The solid oxygen α phase is based on the AFM H geometry.

the O_2-O_2 dimer system in porous materials [8–10]. Because the local molecular arrangement in α and β phases can be regarded as the AFM H geometry, analogous to the dimer case, change in the packing structure of solid oxygen is expected to be realized by applying ultrahigh magnetic fields.

In this Letter, we measured the magnetization (M) and magnetotransmission spectra of the α phase of solid oxygen in ultrahigh magnetic fields of up to 193 T to explore experimentally the magnetic field-induced phase transition of solid oxygen. As well as the magnetization measurement, optical spectroscopy is a powerful method for detecting phase transitions in ultrahigh magnetic fields [11].

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 α oxygen was grown inside the sample cell in which the internal gas was substituted with high-purity oxygen (99.999%) [13]. For the magnetization measurements, the inductive method using a parallel twin-pickup coil was employed [14]. The antipolarized twin-pickup coil cancels out the huge inductive voltage generated by the external magnetic fields, allowing the magnetization signal from the sample inserted in one side of the pickup coil to be measured. The sample was kept at the temperature of liquid ^{4}He (4.2 K) during the magnetization measurements. For the magnetotransmission spectroscopy, a high-speed streak camera with a polychromator was used [13]. 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 Supplemental Material S1 [15].

Figure 2(a) shows the time (t) dependence of the pulsed magnetic field and dM/dt signal of the solid oxygen α phase. The magnetization was measured up to a field of 129 T at 4.2 K. The two distinct dM/dt peaks in the up and down sweeps of the field (indicated by red and blue arrows, respectively) correspond to abrupt changes in the magnetization. A magnetization curve was obtained by integrating the dM/dt signal [Fig. 2(b)]. The initial slope is calibrated with the values reported in Ref. [4]. The fluctuation of the dM/dt signal at 3.5–5.8 μs is caused by experimental error and remains in the magnetization. The magnetization value in the down sweep of the pulsed magnetic field has a particularly large error bar [Fig. 2(b)]; the homogeneity and reproducibility of the magnetic field are reduced for the down sweep because of the coil destruction. However, the magnetization jumps at 125 T in the up sweep and 72 T in the down sweep are reproducible, and hence, correspond to intrinsic phenomena. This finding clearly shows that the field-induced phase transition of the solid oxygen α phase takes place in ultrahigh magnetic fields greater than 120 T. The pronounced hysteretic behavior suggests that the phase transition is first order.

Figure 3(a) shows the two-dimensional transmission spectra image of α oxygen at 21.6 K and the waveform of the pulsed magnetic field up to 128 T as a function of time. The transmission, I/I_0, is represented 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. At zero magnetic field, the transmission is small at 2.15–2.20 eV due to the bimolecular transition of solid oxygen [16–19]. At near the highest magnetic field, 128 T (2.8 μs), the transmission of the α oxygen unexpectedly increases over the whole photon energy range. When the magnetic field decreases, the transmission
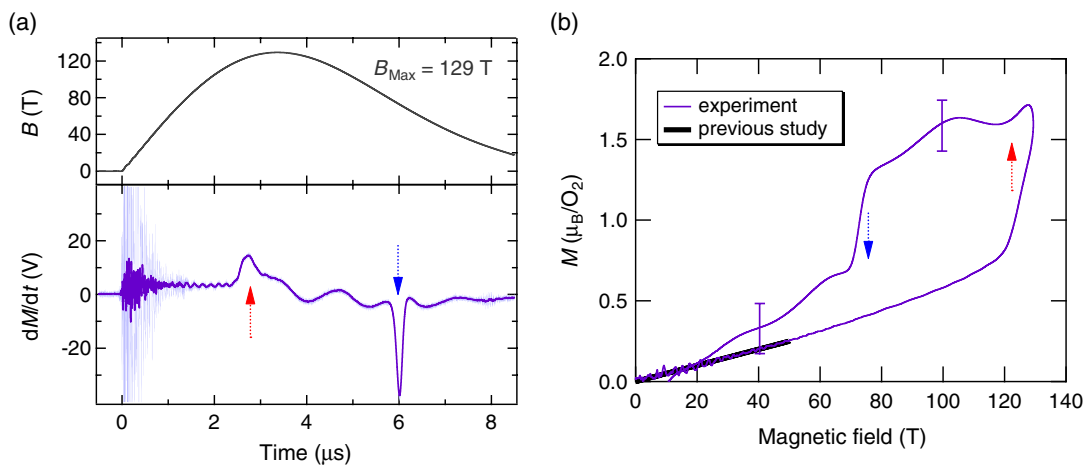

FIG. 2 (color online).   (a) Time dependence of the magnetic field B and dM/dt signal from the twin-pickup coil. The light purple curve is the raw data and the dark purple curve is the result of the numerical smoothing process for the same data. (b) Magnetization curve obtained by integrating dM/dt shown in Fig. 2(a). The initial slope is calibrated with a value from a previous study [4]. The estimated error bars are shown for the data of the down sweep of the pulsed magnetic field. Distinct magnetization jumps are observed in the up (red arrow) and down (blue arrow) sweeps.
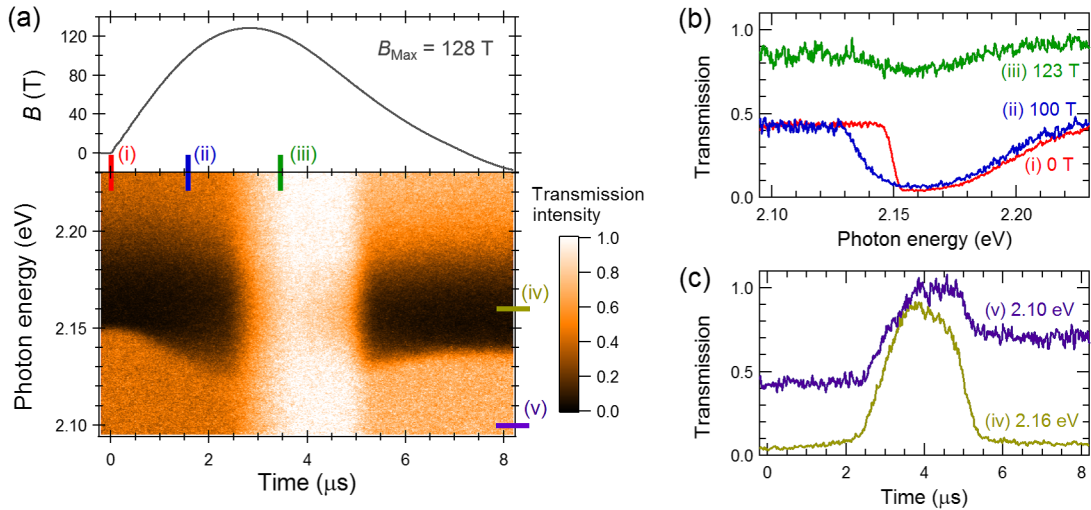
FIG. 3 (color online).   (a) Two-dimensional transmission spectra of the solid oxygen α phase at 21.6 K and the waveform of the pulsed magnetic field up to 128 T are shown as a function of time. The transmission intensity is represented on a color scale. The labels from (i) to (v) show the position of the cross sections in Figs. 3(b) and 3(c). (b) Transmission spectra obtained from the time cross section in Fig. 3(a). The magnetic field intensity is shown for each spectrum. (c) Time dependences of the transmission obtained by the photon energy cross section in Fig. 3(a). The photon energy is shown for each spectrum.

decreases again at about 60 T. These critical fields are close to those of the phase transition observed in the magnetization measurements; hence, this anomalous optical behavior is likely to be connected with the magnetic phase transition.

Figures 3(b) and 3(c) show the cross section of the two-dimensional transmission spectra by time and photon energy, respectively. When the field is less than 100 T (i → ii), the shape of the transmission spectrum changes around only 2.14 eV. This peak deformation is caused by the orbital Zeeman effect of the bimolecular absorption [13,16–19]. As the field passes through its maximum (ii → iii), the transmission at all photon energies increases, and the bimolecular absorption is considerably diminished. The change in the transmission is clearly shown in cross sections (iv) and (v) in Fig. 3(c). At a photon energy of 2.10 eV in cross section (v), the effect of the bimolecular absorption is negligible. In both cross sections (iv) and (v), independent of the existence of the bimolecular absorption, the transmission rapidly increases at 2.5 μs (127 T) and decreases again at 5.2 μs (61 T). The positions almost correspond to the transition field values obtained from the M curve in Fig. 2(b).

The magnetic field dependences of the normalized transmission at 2.10 eV are shown in Fig. 4. Experiments with different maximum fields from 117 to 193 T were conducted at temperatures around 20 K. When the maximum field is lower than 117 T, no change is observed in the transmission. At fields greater than 128 T, the transmission changes at near the maximum field with large hysteresis. As the maximum field increases from 128 to 193 T, the hysteresis loop becomes larger. This maximum field dependence of the hysteresis suggests that the

relaxation time of the phase transition is as long as the duration time of the pulsed field, several microseconds.

Now let us discuss the origin of the observed phase transition of the α oxygen. The abrupt increase in the magnetization suggests that the AFM long range order is disturbed and the spins of O_2 molecules are forced to align
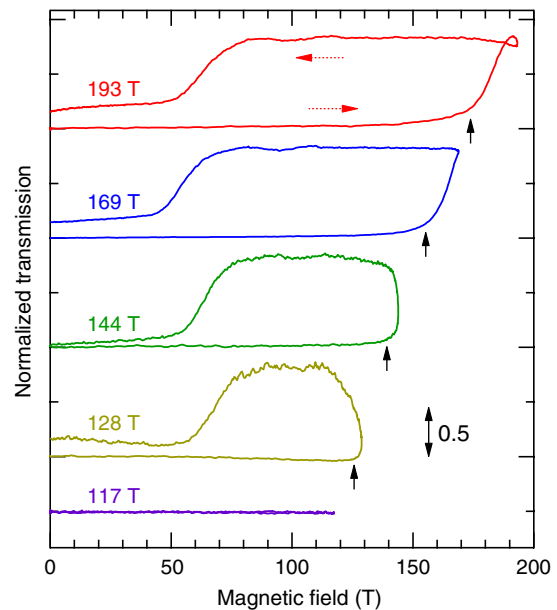

FIG. 4 (color online).   Normalized transmission intensity at 2.10 eV in pulsed magnetic fields with different maximum field strengths and initial temperatures of 193 T and 19.1 K (red), 169 T and 11.1 K (blue), 144 T and 12.6 K (green), 128 T and 21.6 K (yellow), and 117 T and 19.9 K (purple). Abrupt increases in the transmission are indicated by arrows.

parallel to the magnetic field. This affects the bimolecular absorption; bimolecular absorption cannot occur when there are no AFM O_2 pairs [13,16–20]. Therefore, in addition to the magnetization jump, the significant suppression of the bimolecular absorption shown in Fig. 3(b) indicates that the magnetization of the O_2 molecules is close to the saturation at around 123 T. However, it can be said that the transition is not fully completed in this field range because the magnetization remains to increase and the bimolecular absorption has the finite intensity. As seen in Fig. 4, the phase transition is likely to complete at around 160 T for the sweep speed in the present Letter. The magnetization is also expected to reach the saturation in the high magnetic fields.

It is worth noting that the magnetized α oxygen may have a different crystal structure from that of the AFM ordered phase at low magnetic fields. Similar to the O_2-O_2 dimer case as before mentioned, the O_2 molecules can be rearranged to gain exchange energy when they are magnetized. Therefore, a structural change is expected to occur in the ultrahigh magnetic fields. The structural transition explains the observed first order phase transition with large hysteresis.

Next, we discuss how the field-induced structural transition explains the unusual abrupt increase in the transmission shown in Figs. 3 and 4. Actually, a similar phenomenon is observed at the β-γ phase transition at zero field when the temperature is changed. Figure 5 shows that the optical transmission at 2.10 eV changes dramatically at the transition. This phenomenon originates from the change in the classical light scattering at the crystal domain boundaries [2]. In the β phase, the transmission is very small because of the multidomain structure with anisotropic crystal symmetry (rhombohedral). When the γ phase appears, the light scattering significantly reduces because the γ phase has an isotropic cubic structure and isotropic optical properties, which suppress the light scattering at the domain boundaries. The change in transmission can also be directly observed with the naked eye; the β phase looks

opaque and dark, like frosted glass, whereas the γ phase appears almost transparent.

Because the phenomena observed for the field-induced transition (Figs. 3 and 4) and the temperature driven β-γ transition (Fig. 5) are similar, it is suggested that the crystal structure changes from the anisotropic (monoclinic in α phase) to the isotropic one by the magnetic fields. The improvement of the crystal symmetry significantly decreases the scattering of incident light at the domain boundaries of the crystal and increases the transmission. The change in the crystal structure at the field-induced transition is consistent with the large hysteresis and the slow relaxation time in microsecond range. When we compare the transition width observed in the magnetization [Fig. 2(a)] and that in the optical transmission [cross section (v) in Fig. 3(c)], the latter seems to be slightly broader. However, since the experimental conditions (temperature and the pulse duration of the field) are not exactly the same in the two experiments, the detailed quantitative discussion is difficult to be made in this Letter.

Another question one may come up with is what kind of the crystal structure is realized in the ultrahigh magnetic fields. In the O_2-O_2 dimer system, AFM H geometry is not favored and FM S or X geometries are induced [5–7]. However, in three-dimensional solid oxygen, the optimized packing structure is not as simple as that of the dimer system, and it could result in new geometrical coupling. At least, the AFM parallel packing structure of the α phase is expected to be unstable in the field-induced phase. In all phases of solid oxygen, except for the rotationally disordered γ phase, O_2 molecules are aligned in the parallel geometry [2,21–26]. Therefore, the field-induced phase is a previously unknown phase with a highly symmetrical, possibly cubic, crystal structure.

In conclusion, we have performed magnetization measurements and magnetotransmission spectroscopy on solid oxygen α phase using ultrahigh magnetic fields. Above the critical field around 120 T, an abrupt increase in the magnetization occurs with the change in the crystal structure. We propose that the O_2 molecules rearrange from the original parallel geometry and adopt a high-symmetry crystal structure, that could be cubic, with a high magnetic susceptibility. This field-induced phase transition is a clear demonstration of the strong spin-lattice coupling inherent in the solid oxygen. To understand the field-induced phase further, detailed theoretical calculations would help to clarify the possible arrangement of molecules and the resultant crystal structure.
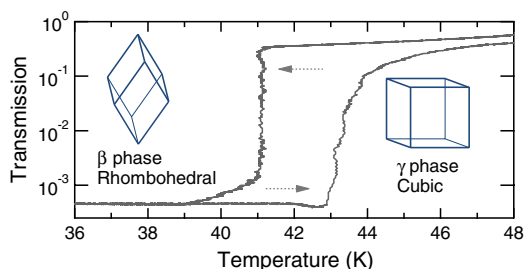
FIG. 5 (color online). Temperature dependence of the transmission of light at 2.10 eV, near the β-γ phase transition. When the rhombohedral β phase is converted to the cubic γ phase, optical anisotropy disappears and the light scattering from the domain boundary is suppressed.

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