**H-T phase diagram of solid oxygen**

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Comprehensive magnetic-field-temperature (H-T) phase diagram of solid oxygen including the θ phase is discussed in the context of the ultrahigh-field measurement and the magnetocaloric effect (MCE) measurement. The problems originating from the short duration of the pulse field, nonequilibrium condition and MCEs, are pointed out and dealt with. The obtained phase diagram manifests the entropy relation between the phases as $S_0 \sim S_\alpha < S_\beta << S_\gamma$.

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I. INTRODUCTION

In the family of elemental solids, solid oxygen shows characteristic properties due to the magnetic moment of O$_2$ [1–3]. The exchange interaction between O$_2$ molecules contributes to condensation energy in addition to the van der Waals interaction. The strength of the exchange interaction greatly depends on the alignment of O$_2$ molecules [4, 5], indicating that the packing structure of solid oxygen is tuned by its magnetic ground state. Moreover, solid oxygen is the only antiferromagnetic (AFM) insulator composed of single element [8].

Thus, the phase diagram of solid oxygen is a unique network of solid oxygen including the θ phase is tuned by its magnetic ground state. The strongest magnetic field is applied to solid oxygen, it is natural to change the packing structure for smaller AFM interaction. Recently, first-principle calculation also supports that the θ phase should have a crystal structure where molecules are packed with the canted alignment (cubic, Pm3m) [3].

The thermodynamical H-T phase diagram of solid oxygen including the θ phase has not yet been clarified. The biggest obstacle is the requirement of the ultrahigh magnetic field above 100 T. Such a high field is generated only by using the destructive pulse technique [14]. Because of the short duration of the field, the phase transition occurs with large hysteresis indicating non-equilibrium condition [11, 12]. In addition, temperature of the sample could change by the magnetocaloric effect (MCE) during the adiabatic magnetization [13]. To obtain the thermodynamical phase boundary, these problems have to be dealt with.

In this paper, the thermodynamical H-T phase diagram of solid oxygen is summarized as a compilation of the experimental works; STC [11, 12, 15] and adiabatic MCE [16]. In Sect. II, three major problems, (i) nonequilibrium, (ii) irreversible MCE, and (iii) reversible MCE are explained with results. In Sect. III, sweep-speed dependence of the transition field is classified as a guide for dealing with the problems. In Sect. IV, the H-T phase diagram is carefully constructed with avoiding the problems. We discuss the entropy relation between the phases in terms of the obtained phase diagram. In Sect. V, conclusion is stated.

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II. RESULTS OF THE FIELD-INDUCED PHASE TRANSITIONS

A. α-θ and β-θ transitions in STC

The θ phase has been confirmed by the magnetization and magneto-optical measurements [11, 12]. Representative results of the α-θ phase transition are shown in Fig. 1. Initial temperature $T_0$, measured immediately before
observed. The transition fields in up and down sweeps (Fig. 1(a)) and transmitted-light intensity \( I \) (Fig. 1(b)) are observed. The transition fields in up and down sweeps \((H_c^+, H_c^-)\) are shown by the arrows. As increasing \( H_{\text{max}} \), hysteresis becomes larger since the phase transition cannot follow the faster sweep of the pulsed field. As a result, \( H_c^+ \) and \( H_c^- \) are not uniquely defined even at the same \( T_0 \). This is the problem (i), effect of non-equilibrium.

In Fig. 1(a), the down sweep of the magnetization curve \((H_{\text{max}} = 129 \, \text{T}, \, T_0 = 4 \, \text{K})\) accords with the \( \beta \) phase despite the initial phase is \( \alpha \). This is due to the irreversible heating during the \( \alpha-\theta \) phase transition \(15\). Dissipation related to the first-order phase transition (hysteresis loss and dissipative motion of domain walls) results in the heating effect. Namely, \( T \) differs from \( T_0 \) after the \( \theta \) phase appears. This is the problem (ii), irreversible MCE. Fortunately, the irreversible MCE is relevant only when \( H_{\text{max}} \) is relatively higher since it is proportional to the amount of the induced \( \theta \) phase. The change of \( T \) is not significant if the phase transition barely occurs like in the condition of \( H_{\text{max}} = 124 \, \text{T} \) where the down sweep of the magnetization accords with the \( \alpha \) phase.

**B. \( \beta-\gamma \) and \( \alpha-\beta \) transitions observed in MCE**

The \( \beta-\gamma \) and \( \alpha-\beta \) transitions have been observed by the adiabatic MCE measurement \(16\). Figure 2 shows the results near the (a) \( \beta-\gamma \) and (b) \( \alpha-\beta \) phase boundaries. When these transitions occur in the adiabatic condition, \( T \) changes along the phase boundary. Here, entropy stays constant by balancing the \( T \) and the fractions of the coexisting phases. Since the measurement of the STC is adiabatic, \( T \) changes from \( T_0 \) if the \( \beta-\gamma \) and \( \alpha-\beta \) phase transitions are induced. This is the problem (iii), reversible MCE. The reversible MCE is serious only beneath the \( \beta-\gamma \) and \( \alpha-\beta \) phase boundaries. If no phase transition occurs, \( \Delta T \) is less than 1 K even at 50 T \(16\).

**III. SWEEP-SPEED DEPENDENCE OF \( H_c \)**

We classify the sweep-speed \( v \) dependence of the transition fields \( H_c \), as a guide for dealing with the problems. In this paper, the superscript \(+ (−)\) is used for the up (down) sweep. Figure 3(a) shows the definitions of \( H_c^+ \) and \( v^+ \), which follow the way of Ref. 12. \( H_c \) is defined by the extrema in \( dM/dt \) or \( dM/dt \). \( v \) is self-consistently defined as the averaged sweep speed between the timings at \( H = H_0 \) and \( H_c \). \( H_0 \) is the expected \( H_c \) in a quasi-static process \((v = 0 \text{ in Fig. 3(b)})\). In this definition, \( v \) is obtained as the sweep speed during the phase transition proceeds.

For the \( \alpha-\theta \) phase transition, \( H_c \) is plotted as a function of \( v \) in Fig. 3(b). The data at \( T_0 < 22 \, \text{K} \) are plotted and equally treated since \( H_c \) seems to be independent on \( T_0 \) in this temperature range. By the linear fitting, we obtained the \( v \) dependence of \( H_c \) as

\[
H_c^+ = 0.69(5) \, v^+ + 108(2) \, \text{T},
\]
\[
H_c^- = -0.05(6) \, v^- + 72(2) \, \text{T}.
\]

By taking the slope 0.69 for up sweep, we corrected \( H_c^+ \) to the limit of \( v = 0 \). The corrected transition field \( H_{00}^+ \) corresponds to the value expected at quasi-equilibrium condition. For discussing the thermodynamical phase diagram, \( H_{00}^+ \) is more appropriate since the effect of non-equilibrium is suppressed. In this study, we applied this correction for all temperature range assuming that the \( \beta-\theta \) phase transition also follows the same \( v \) dependence. For the down sweep, the correction was not applied since \( B_c^- \) does not depend on \( v^- \) greatly.
and \( \beta \) the self-consistent way.

The fraction of the field-induced irreversible MCE is considered to be proportional to the temperature change after the field-induced phase transition, originating from the problem (i) is greatly suppressed in this condition. The averaged transient hysteresis loss was observed [15].

Summarizing them, the entropy relation is obtained as

\[
S(0) - S(T) = \frac{1}{2} \Delta S_{\alpha\theta} - \frac{1}{2} \Delta S_{\beta \gamma}.
\]

FIG. 3. (a) Graphical definition of the sweep speed \( v = \Delta H/\Delta t \). (b) \( v \) dependence of the transition field [12]. Circles and triangles show the results of the magnetization and optical measurements, respectively. The color scale shows \( T_b \) for each plot. Dotted line shows the linear fitting of \( H_c \). \( H_0 \) is the expected \( H_c \) at \( v = 0 \), and used for the definition of \( v \) in the self-consistent way.

IV. PHASE DIAGRAM

In this section, the \( H-T \) phase diagram is corrected from Fig. 3(a) to 3(d) by dealing with the problems one by one. Figure 3(a) is the naively obtained phase diagram, where \( H^+_c \) and \( H^-_c \) are plotted as a function of \( T_0 \). The \( \beta-\gamma \) and \( \alpha-\beta \) phase boundaries obtained by the adiabatic MCE measurement are shown by solid curves [12]. Deviation of \( H^+_c \) is due to the non-equilibrium of the \( \alpha-\theta \) and \( \beta-\theta \) phase transitions [11] [12]. The \( v \) dependence of \( H^+_c \) has to be taken into account for further discussions.

Figure 3(b) shows the corrected phase diagram plotting \( H^+_c \) instead of \( H^+_c \). By the correction, the deviation originating from the problem (i) is greatly suppressed. For discussing the thermodynamical phase diagram, it is usual to read the center of hysteresis as \( H^{cve}_c = (H^+_c + H^-_c)/2 \). However, we should be careful for the temperature change after the field-induced phase transition. Especially after the \( \alpha-\theta \) phase transition, irreversible heating as much as 700 J/mol related to the hysteresis loss was observed [12].

To avoid the effect of irreversible MCE (problem (ii)), data plots obtained only with slower \( v (15 < v^+ < 30 \text{ T}/\mu\text{s}) \) are selected in Fig. 3(c). Slower \( v \) implies that the phase transition barely occurs at the top of the field. Irreversible MCE is considered to be proportional to the fraction of the field-induced \( \theta \) phase. Therefore, the temperature difference between the up and down sweeps are greatly reduced in this condition. The averaged transition field \( H^{cve}_c \) is plotted by black star. The Clausius-Clapeyron equation

\[
\frac{dT_c}{dH_c} = -\frac{\Delta M}{\Delta S}
\]

suggests that the obtained steep phase boundary means large \( \Delta M \) and small \( \Delta S \).

Here, we quantitatively discuss the entropy relation between the \( \alpha, \beta, \gamma \), and \( \theta \) phases. The slope of the phase boundaries are roughly estimated as \( 5 < |dT/dB|_{\alpha\theta} < 1 \) and \( |dT/dB|_{\beta\gamma} < 10 \) in the units of \( K/T \). The differences of the magnetization are roughly estimated as \( \Delta M_{\alpha\theta} = 1.2 \mu_B/O_2 \) and \( \Delta M_{\beta\gamma} = 1 \mu_B/O_2 \). Here, we assumed that the magnetization of the \( \theta \) phase is saturated (\( M_\theta = 2 \mu_B/O_2 \)). Based on Eq. (3), the entropy differences are obtained as \( |\Delta S|_{\alpha\theta} < 0.16 R \) and \( -0.67 R < |\Delta S|_{\beta\gamma} < -0.07 R \). At zero field, the entropy relation between the \( \alpha, \beta, \) and \( \gamma \) phases are already known as \( S_\alpha < S_\beta << S_\gamma \) with the differences of \( \Delta S_{\alpha\beta} = 0.47 R \) and \( \Delta S_{\beta\gamma} = 2.04 R \).

Summarizing them, the entropy relation is obtained as \( S_\theta \sim S_\alpha < S_\beta << S_\gamma \). In the following, we assume the \( \gamma \) phase survives at high fields [18] and discuss how the four phases connect each other in the \( H-T \) phase diagram.

Large \( |\Delta S|_{\beta\gamma} \) suggests that the \( \gamma-\theta \) phase boundary is flat. In addition, \( |\Delta M|_{\beta\gamma} \) would be almost zero since the magnetizations of the \( \theta \) and \( \gamma \) phases almost saturate at 150 T. Therefore, \( \theta-\gamma \) phase boundary has to be completely flat as shown by the gray dashed line in Fig. 3(c). Here, the \( \beta-\gamma-\theta \) triple point is not clear since the extrapolated \( \beta-\gamma \) phase boundary does not smoothly connect to the \( \theta-\gamma \) boundary.

For explaining the \( \beta-\gamma-\theta \) triple point, the reversible MCE (problem (iii)) has to be taken into account. The schematic MCE curve is shown in Fig. 3(a). When the magnetic field passes the \( \beta-\gamma \) phase boundary in the adiabatic condition, \( T \) decreases along the phase boundary with increasing the fraction of the \( \gamma \) phase. For example, in the case of \( T_0 = 42 \text{ K}, 100 \text{ T} \) is necessary for the entire phase transition from the \( \beta \) to \( \gamma \) phase [10]. That means the plots beneath the \( \beta-\gamma \) phase boundary are cooled down to the \( \beta-\gamma-\theta \) triple point with phase coexistence. Finally at the \( \beta-\gamma-\theta \) triple point, the \( \beta \) phase will transform to the \( \theta \) phase, which is detected in the experiment. At higher field than the triple point, the MCE curve will follow the \( \gamma-\theta \) phase boundary with phase coexistence. However, this phase coexistence cannot be confirmed by the magnetization and optical spectroscopy since the \( \gamma \) and \( \theta \) phases show similar results in these measurements.

The same behavior of MCE would occur also for the \( \alpha-\beta \) phase boundary. Therefore, the data plots around 20 K would also reach to the \( \alpha-\beta-\theta \) triple point as shown in Fig. 3(b). At the triple point, the \( \alpha \) and \( \beta \) phases wholly transform to the \( \theta \) phase. When the \( \beta-\gamma \) and \( \alpha-\beta \) phase transitions are not involved (\( T_0 < 15 \text{ K} \)), the effect of the reversible MCE is less than 1 K and negligible [16].

Finally, we propose the \( H-T \) phase diagram of solid oxygen as Fig. 3(d). Here, we assume that the data plots around 40 K and 20 K get together at the triple points. The \( \theta-\gamma \) transition (solid-plastic transition) is expected to occur at 31 K. This is close to the value of the solid-plastic transition of N\(_2\) (\( \alpha-\beta \) transition, \( T_{\alpha\beta} = 35.6 \text{ K} \)) [17].

The thermodynamical \( \alpha-\theta \) transition field is obtained
FIG. 4. \(H-T\) phase diagram of solid oxygen. (a) \(H^+\) and \(H^-\) are plotted as a function of \(T_0\) without any modifications. Circles and triangles show the results of the magnetization and optical measurements, respectively. (b) \(H^0\) is plotted instead of \(H^+\). (c) The data points obtained in slower sweep speed (15 < \(v^+\) < 30 T/\(\mu\)s) are selected. The averaged transition field \(H^\text{ave} = (H^+ + H^-)/2\) is plotted by black star with the guiding curve. The gray dashed line is the \(\theta-\gamma\) phase boundary expected from the entropy relation. (d) Proposed \(H-T\) phase diagram of solid oxygen. The reversible MCEs along the \(\beta-\gamma\) and \(\alpha-\beta\) phase boundaries are taken into account.

V. CONCLUSION

The thermodynamical \(H-T\) phase diagram of solid oxygen including the \(\theta\) phase was proposed as Fig. 4(d). The phase diagram was obtained by analyzing the results of the magnetization, optical, and adiabatic MCE measurements with avoiding the problems originating from the short duration of the field. Using the Clausius-Clapeyron equation, the entropy relation between the phases was obtained as \(S_\theta \sim S_\alpha < S_\beta << S_\gamma\).

The corrections of the phase diagram applied in Figs. 4 are abstracted as follows. From (a) to (b), \(H^+\) was corrected to \(H^0\) by using the \(v\) dependence of \(H^+\) for suppressing the effect of (i) non-equilibrium. From (b) to (c), only the data obtained in slower \(v\) were collected for reducing the effect of (ii) irreversible MCE. Here, \(H^\text{ave}\) measurements are important for revealing the whole picture of the \(\theta\) phase and for further understanding of oxygen.

FIG. 5. Expected MCE curves beneath the (a) \(\beta-\gamma\) and (b) \(\alpha-\beta\) phase boundaries.
was introduced for discussing the thermodynamical phase boundary. From (c) to (d), the effect of (iii) reversible MCE was taken into account for the consistency of the $\beta$-$\gamma$-$\theta$ triple point. In the adiabatic condition of the STC, $T$ is expected to decrease along the $\beta$-$\gamma$ and $\alpha$-$\beta$ phase boundaries and to reach to the triple points.

The ground state of oxygen obviously depends on the external magnetic field since $\text{O}_2$ is a magnetic molecule. The obtained $H$-$T$ phase diagram will contribute for discussing the thermodynamical stability of oxygen. Potentially, it could lead to controlling the chemical activity of oxygen by magnetic field, during the biological reaction or material processing [23, 24].

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