

Kagome lattice of oxygen in N₂-O₂ system

The purpose of our research is to study for new magnetic orders of the oxygen molecule O₂. O₂ is a molecular magnet with a magnetic moment of 2μ_B perpendicular to the molecular axis. In the pressure-temperature (*P-T*) phase diagram of oxygen, rich polymorphism with a unique magnetic order arises from the magnetic interaction between O₂ molecules. We previously found a new solid phase in the pressure-composition phase diagram of the N₂-O₂ binary system [1]. This phase has a hexagonal structure and does not occur in pure O₂ or pure N₂. By Rietveld refinement (Fig. 1), we determined the structure of this phase to be a hexagonal lattice (*P6/mmm*) with seven molecules in the unit cell. In this structure (Fig. 2), the molecules occupy three different sites. Three molecules in the 6(*i*) site form a kagome lattice and their molecular axes are almost parallel to the *c* axis because of orientational ordering. Supporting evidence for the formation of the kagome lattice in O₂ has been obtained from other experimental results [1].

The spin kagome lattice is a fascinating system among the frustrated spin systems and its magnetic property has attracted much attention from many condensed-matter physicists. Therefore, our interest is focused on the hexagonal phase of the N₂-O₂ binary system because this phase is a promising candidate for the *S* = 1 kagome lattice system. In order to investigate the stability and magnetic property of the hexagonal phase, X-ray diffraction experiments and magnetic measurements were performed under high-pressure and low-temperature conditions. In the present work,

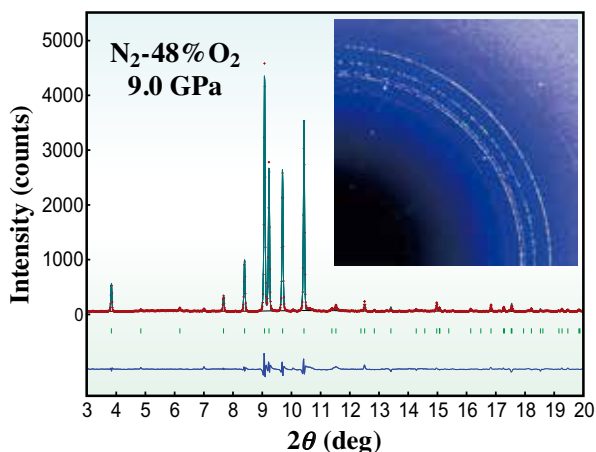


Fig. 1. Diffraction pattern and image of the hexagonal phase of 48%O₂ sample at 9.0 GPa. By Rietveld analysis, the pattern was well explained as a structure model of S.G.: *P6/mmm*.

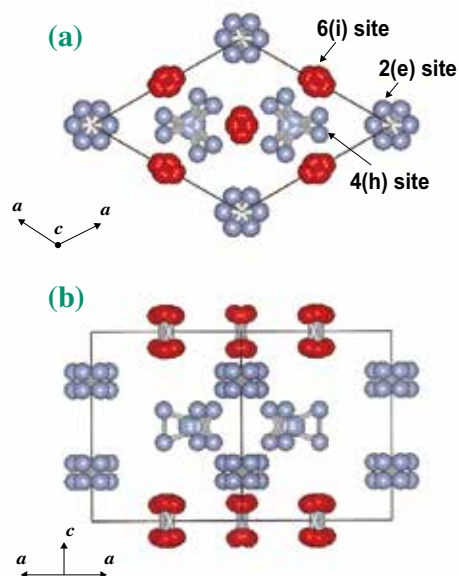


Fig. 2. Structural model of the hexagonal (*P6/mmm*) phase, showing views from the *c* axis (a) and the [110] direction (b). The rotational disorder of molecules was simulated by placing 1/8 or 1/12 atom into the 24(*r*) site for each molecule. Molecules in the 6(*i*) site (colored in red) form a kagome lattice in the *c* plane, and their molecular axes are almost parallel to the *c* axis because of the orientational order, while molecules in the other sites (colored in gray) are freely rotating.

the sample composition of N₂-48 mol% O₂ was adopted because for this composition the hexagonal phase is stable in a wide pressure range [1]. Powder X-ray diffraction experiments were conducted using an angle-dispersive method with a DAC at SPring-8 BL10XU. Magnetization measurements were performed using the MPMS and a pencil-type DAC.

From the X-ray diffraction experiments, we obtained the phase diagram shown in Fig. 3(a) [2]. Upon cooling to 90 K at a low pressure of 1 GPa, the fluid phase transformed to the hexagonal phase via the well-known hcp phase of β-N₂ and the cubic (*Pm3n*) phase of γ-O₂ or δ-N₂. Upon further cooling, the hexagonal phase transformed to a monoclinic phase at 60 K. At 3 GPa, each transition temperature was increased. Above 4 GPa, the hexagonal phase (*P6/mmm*) transformed to an orthorhombic phase prior to its transformation to the monoclinic phase. The hexagonal-to-orthorhombic phase transition was second-order-like and was indicated by the broadening of the diffraction lines.

The phase diagram suggests that the hexagonal phase with the kagome lattice is stable in a relatively wide temperature and/or pressure range. The β phase ($R\bar{3}m$) of pure oxygen, which consists of a spin triangular lattice, also transforms into a monoclinic or orthorhombic phase at a low temperature to eliminate the geometrical frustration.

Structure analyses were conducted for patterns of the orthorhombic and monoclinic phases [2]. The unit cell of the orthorhombic phase is derived from an orthorhombic deformation of the hexagonal phase and is equivalent to a twofold hexagonal phase unit cell. From classical molecular dynamics (MD) simulations and Rietveld refinement, the phase was explained as the $Cmmm$ space, the molecular axis of O_2 was almost parallel to the c axis, and the N_2 molecules were in a state of rotational disorder. These facts suggest that the transition to the orthorhombic phase is not driven by the ordering of the rotational motion of molecules. The structure of the monoclinic phase was also analyzed by the same process. An MD simulation at 10 K indicated orientational ordering for not only O_2 but also N_2 molecules. The $P2_1/a$ space group accounted for the results of the simulation. The results

of the Rietveld refinement suggest that the diffraction pattern is due to the monoclinic $P2_1/a$ phase. The transition to the monoclinic phase may result from the ordering of the rotational motion of N_2 molecules. The transition from the hexagonal phase to the monoclinic phase was accompanied by a distortion of the kagome lattice.

Figure 3(b) shows the representative temperature changes of the magnetic susceptibility χ of the sample [2]. At a low temperature, χ shows a sudden drop. The onset temperature T_A of the drop is 38 K at 0 GPa and increases with increasing pressure. The estimated reduction of χ , $\Delta\chi$, is 58.1×10^{-6} emu/g and decreases with increasing pressure. The behavior of χ suggests a change in the magnetic property of the sample such as a transition to an antiferromagnetic state. It was found that the magnetic anomaly at 1 GPa corresponds well to the cubic-hexagonal phase transition. Therefore, the anomaly should be due to the structure phase transition. The results suggest that the hexagonal phase has a specific magnetic ordered state, arising from the molecular magnetic moment of O_2 . These results provide evidence for the formation of the kagome lattice in O_2 in the hexagonal phase.

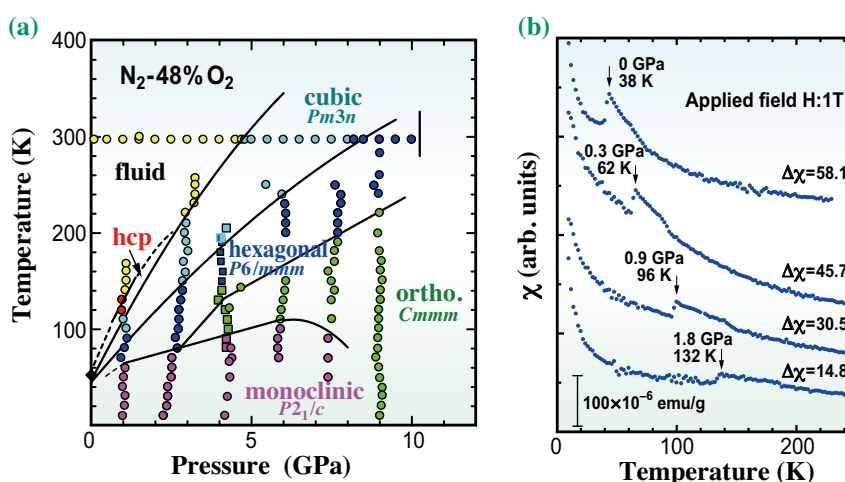


Fig. 3. (a) Pressure-temperature phase diagram of N_2 -48 mol% O_2 sample. Circles and squares correspond to cooling and heating cycles, respectively. (b) Representative temperature changes in the sample magnetic susceptibility χ .

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