Nanoscale Ice-Type Structural Fluctuation in Spinel Titanates

To explore the structural ice-type state, we substituted nonmagnetic Mg ions for Ti ions in spinel titanates $MgTi_2O_4$ and measured the X-ray diffraction, neutron atomic pair distribution function, and extended X-ray absorption fine structure. We found that a tiny amount of Mg substitution caused the sudden collapse of the tetragonal phase and resurrection of the cubic phase. An analysis of the two-body correlation revealed that the displacement-type ice state, in which two Ti atoms are displaced inward and the other two Ti atoms are displaced outward in the tetrahedra in the pyrochlore lattice, is created during the cubic phase.

Geometrical frustration is a central research topic in the field of condensed matter physics and have given rise to interesting physical properties. The first example of a frustrated system was given as crystalline ice, as reported by Pauling [Fig. 1(a)] [1]. The ice rule, which states that the oxygen is coordinated to two covalently bonded hydrogens and two hydrogen-bonded hydrogens, causes the disorder state in the hydrogen atoms. Anderson applied this ice rule to the spin and charge degrees of freedom. The spin-ice state, in which the spin has a two-in-two-out-type local order, was discovered in pyrochlore titanates [Fig. 1(b)] [2].

To pursue ice physics, realizing the structural ice-type state in strongly correlated electron systems that have high controllability and many degrees of freedom is essential. The structural ice-type state (i.e., "displacement-type ice") is defined so that two atoms are displaced inward and the other two atoms are displaced outward in the tetrahedra in the pyrochlore lattice [Fig. 1(c)]. The figure shows the original positions (blue) and displaced positions (green) of atoms. Here, the lengths of the red, gray, and blue bonds become short, intermediate, and long, respectively. This displacement follows the ice rule.

In the d^1 electronic system, one valence electron can create a spin singlet pair and a single bond. This spin-lattice coupling can be a driving force for creating the structural two-in state in the pyrochlore lattice. Thus, we focused on the spinel titanate, $MgTi_2O_4$ (Ti^{3+} ($3d^1$) $S = 1/2$).

In $MgTi_2O_4$, the structural transition from the cubic phase to the tetragonal phase occurs during cooling at $T_c \approx 260$ K and is also accompanied by a transition to the nonmagnetic state (left side of Fig. 2(a)) [3]. Below T_C, the long and short bonds between the Ti ions are arranged alternately along the *c* axis, as illustrated in the left inset of Fig. 2(a). This Ti atomic displacement follows the ice rule. Unfortunately, this phase transition relieves the frustration originating from the degeneracy of the Ti dimer formation.

To explore the structural ice-type state, we substituted the nonmagnetic Mg ions for Ti ions in $MgTi_2O_4$ and shortened the correlation length of the tetragonal structure. For its detection, we measured the X-ray diffraction (BL-8A and -8B) and the two-body correlation with Ti ions using the neutron atomic pair distribution function (PDF) (J-PARC BL21) and the extended X-ray absorption fine structure (EXAFS) (BL-9A and -12C). By performing nanoscale structural analyses, we found the nanoscale ice-type structural fluctuation in the cubic phase.

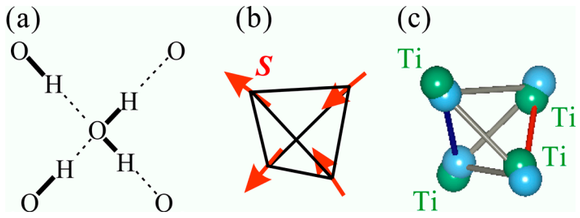

Figure 1: (a) Configuration of H_2O molecules in ice. (b) Spin orientation in the spin-ice state as indicated by the red arrows. (c) Original positions of the atoms (blue spheres) and positions of the displaced atoms (green spheres) in the two-in-two-out-type displacement. The red line indicates the Ti dimer.

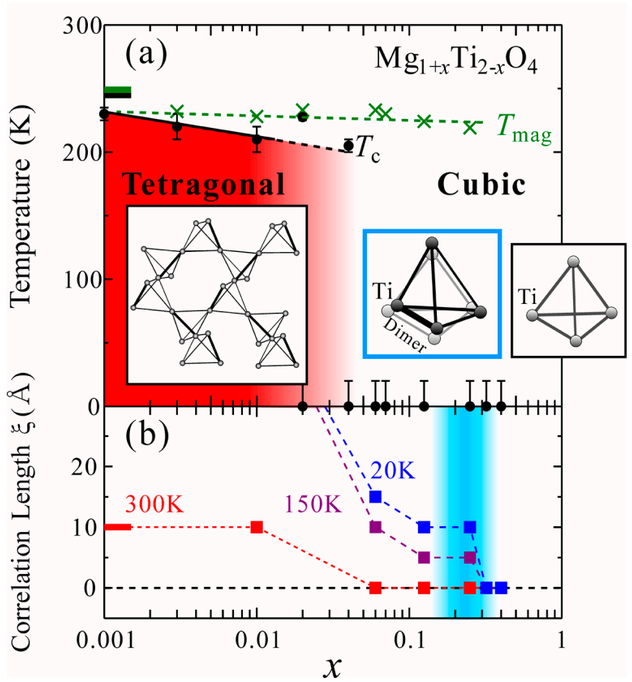

Figure 2: (a) Phase diagram of the lattice structure and the magnetism in $Mg_{1+x}Ti_{2-x}O_4$. The black circles and green crosses indicate the structural transition temperature (T_c) and temperature (T_{mag}) at which the magnetic susceptibility decreases, respectively. The insets illustrate the structure of the Ti tetrahedra. The thick lines indicate the Ti dimer. (b) x dependence of the correlation length ξ of the tetragonal structure obtained by PDF analyses at 20 K (blue), 150 K (purple), and 300 K (red). The blue x region indicates the ice-type state. The thick bars on the left ordinate in (a) and (b) indicate the values at x = 0 [4].

Based on experimental results, we present the phase diagram of $Mg_{1+x}Ti_{2-x}O_4$ in Fig. 2(a) [4]. When x = 0, the tetragonal phase existed below $T_c \approx 260$ K. For x > 0.06, the structural transition temperature T_c dropped to zero, as suggested by the X-ray diffraction measurement. A tiny amount of Mg substitution caused the sudden collapse of the tetragonal phase and the resurrection of the cubic phase. Nevertheless, the reduction of the magnetic susceptibility below T_c was still discernible. The temperature T_{mag}, below which the magnetic susceptibility decreases, remained at ≈ 230 K, indicating the existence of spin-singlet pairs. Indeed, the EXAFS measurement reveals that the two-in-two-out-type displacement of the Ti ions remained at x < 0.32. We estimated the correlation length ξ of the tetragonal structure by PDF analysis [Fig. 2(b)]. The correlation length ξ of this tetragonal structure approached zero in x = 0.25–0.32. The nanoscale fluctuation of the local tetragonal structure and the two-in-two-out-type displacement of the Ti ions existed at x < 0.32 in the cubic phase. The displacement-type ice state was created near x = 0.25, as indicated by the blue x region.

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BEAMLINES

BL-8A, BL-8B, BL-9A and BL-12C

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