Stability of hexamer-type spin excitations in the frustrated spinel Mg$_{1-x}$Cr$_2$O$_4$$_x$

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Abstract. We performed magnetic susceptibility and inelastic neutron scattering measurements on the frustrated spinel Mg$_{1-x}$Cr$_2$O$_4$$_x$ (0 $\leq$ x $\leq$ 0.11). Susceptibility shows that Curie-Weiss temperature is almost independent of x, meaning that exchange interactions sustain. Inelastic neutron scattering reveals that the spin-hexamer excitations also persist with almost the same energy around 4 meV in a lowest temperature phase, whereas the resonance width increases with increasing x. These results suggest that nearest-neighbor Cr\textperiodcentered Cr direct exchange predominantly forms the hexamers regardless of lattice defect and superexchange via Mg and O sites.

1. Introduction

A series of spinel chromates ACr$_2$O$_4$, in which Cr$^{3+}$ ions with spin $S$ = 3/2 form a pyrochlore structure, is well known as a geometrically frustrated system. ZnCr$_2$O$_4$ and MgCr$_2$O$_4$, in which non-magnetic ions Zn$^{2+}$ and Mg$^{2+}$ occupy the A sites, exhibit characteristic dynamical short-range spin clusters in paramagnetic and magnetically ordered phases, called spin molecules [1, 2, 3, 4]. In an ordered phase, the molecules are observed as resonance-like excitations with discrete energies $E$ = 4.5 and 9.0 meV, which are identified to be hexamer and heptamer, respectively [4].

The hexamer-type resonance-like excitations, albeit broadened in energy, interestingly persist even in a spin glass phase in the A-site-substituted Zn$_{0.95}$Cd$_{0.05}$Cr$_2$O$_4$, in which static magnetic long-range order is suppressed [5]. This fact suggests that the hexamer formation does not rely on the magnetic order [5].

In this paper, we further approach an origin of the hexamers by magnetization measurements and inelastic neutron scattering on the A- and O-site-defected Mg$_{1-x}$Cr$_2$O$_4$$_x$ (0.02 $\leq$ x $\leq$ 0.11). The defect with the wider x range is expected to more effectively deform lattice, modify superexchange, and destroy the hexamers than the substitution. However, it is revealed that the hexamers still persist in all the x range.
2. Experiments

Single-crystalline samples of Mg$_{1-x}$Cr$_2$O$_{4-x}$ ($x = 0.02, 0.06, 0.11$) were grown by a floating zone method (4-Xe lamp design, Crystal Systems Corporation) for the first time. The polycrystalline feed rods were synthesized from mixtures of MgO and Cr$_2$O$_3$ under Ar atmosphere by a solid-phase reaction method. Since MgO was inevitably evaporated in our crystal growth, the molar ratio was adjusted to be $(1 - x) \times 1.08 : 1$ with excess MgO. The rods were crystallized with 20 mm/h growth and seeding speeds under 6 atm Ar atmosphere. Then the single crystals with 4 mm diameter and 20 to 30 mm long were obtained. The final molar ratios of Mg to Cr and the resultant $x$ values were confirmed by inductively coupled plasma atomic emission spectroscopy (ICP). The degree of the oxygen defect was assumed to keep the valence of Cr at 3+, since Cr normally takes only 3+ or 6+.

Single-crystalline magnetic susceptibility was measured by a superconducting quantum interference device magnetometer (SQUID: Quantum Design MPMS-5). Single-crystalline neutron scattering experiments were performed on a triple axis spectrometer, AKANE (T1-2), installed at the thermal guide tube of JRR-3, Japan Atomic Energy Agency (JAEA), Tokai, Japan. The incident energy was fixed at $E_i = 19.4$ meV with a horizontal collimation sequence of guide $60' - 60' - 60' -$ blank. Each sample was mounted to use the $(hk0)$ scattering plane, and was cooled in an Al can in a closed-cycle He refrigerator.

3. Results

![Figure 1](image-url)

**Figure 1.** Temperature dependence of field-cooled (FC) magnetic susceptibility (a) and inverse one (b) measured under a magnetic field of 50 Oe. Open circles, open squares and open triangles represent the data for Mg$_{0.98}$Cr$_2$O$_{3.98}$ ($x = 0.02$), Mg$_{0.94}$Cr$_2$O$_{3.94}$ ($x = 0.06$) and Mg$_{0.89}$Cr$_2$O$_{3.89}$ ($x = 0.11$), respectively. The inset in (a) shows temperature dependence data of zero-field-cooled (ZFC) and FC magnetic susceptibility for Mg$_{0.89}$Cr$_2$O$_{3.89}$ ($x = 0.11$).

Figure 1(a) shows the temperature dependence of the field-cooled (FC) magnetic susceptibility measured on Mg$_{1-x}$Cr$_2$O$_{4-x}$ in a magnetic field of 50 Oe. The $x = 0.02$ susceptibility decreases and abruptly drops at Neel temperature $T_N = 12.5$ K with no difference between the zero-field-cooled (ZFC) and FC curves, which is the same as in MgCr$_2$O$_4$. Meanwhile, the $x = 0.06$ and 0.11 susceptibility exhibits a sharp cusp at $T^* = 11.4$ K. The ZFC-FC difference appears below $T^*$, as the $x = 0.11$ curves are shown in the inset in Fig. 1(a).
as the representative, suggesting appearance of a spin-glass-like state. There seems to be also another anomaly at 10 K.

Figure 1(b) shows the temperature dependence of the inverse FC susceptibility. The data between 150 and 300 K is linear, giving the Curie-Weiss temperatures $\Theta_{CW} = -408, -396$ and $-401$ K for $x = 0.02, 0.06$ and 0.11, respectively. Assuming that nearest-neighboring direct exchange interactions $J_1$ are dominant as for $x = 0$ (MgCr$_2$O$_4$), these values correspond to $-4.7, -4.6$ and $-4.6$ meV. All the values obtained above coincide with those for MgCr$_2$O$_4$ ($\Theta_{CW} = -400$ K [6] and $J_1 = -4.6$ meV).

Next, we measured the resonance energy by inelastic neutron scattering. Figures 2(a) and 2(b) show the constant-Q scan data at (1.25,1.25,0) reciprocal lattice unit, where strong diffusive magnetic scattering appears from the hexamers [4]. The resonance-like peak of the hexamers is robustly observed at all the $x$ values, though the broadening is severe at $x = 0.11$. By fitting the data with double Gaussians, the resonance energies (the center positions of Gaussian) are estimated to be 4.7, 4.1 and 4.1 meV, and the resonance widths (full widths at half maximum) are 1.3, 1.8 and 3.3 meV for $x = 0.02, 0.06$ and 0.11, respectively.

4. Discussion

Thus we revealed that $x$ as well as static magnetic ordering/freezing does not influence both the exchange interactions ($\Theta_{CW}$) and the resonance energy in Mg$_{1-x}$Cr$_2$O$_{4-x}$. The defect at A and O sites is expected to substantially deform lattice and many bond angles on superexchange paths via A and O sites. Therefore, this $x$ independency suggests that nearest-neighboring direct exchange interactions predominantly form the hexamers rather than lattice deformation and superexchange. On the other hand, the resonance width increases with increasing $x$ (Figs. 2(a) and 2(b)), suggesting that the hexamers gradually become unstable probably because the lattice deformation and superexchange enhance inter-hexamer correlations.

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