Neutron scattering study of spiral-type spin correlations in the frustrated spinel Mn$_{0.07}$Mg$_{0.93}$Cr$_2$O$_4$

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Abstract. We studied spiral-type spin correlations in Mn$_{0.07}$Mg$_{0.93}$Cr$_2$O$_4$ by single-crystalline neutron scattering. The correlation lengths are evaluated to be 12.7 Å and 4.4 Å along parallel and perpendicular to the propagation vector, respectively. The spiral rotational plane is estimated to be the proper-screw type rather than the cycloid-screw one. This fact suggests that Mn moments stabilize the cycloidal structure, generating the ferroelectricity in the parent material MnCr$_2$O$_4$.

1. Introduction

A series of the spinel-type chromates $ACr_2O_4$ is a well-known geometrically frustrated system, in which Cr$^{3+}$ ions (spin $S = 3/2$) construct a pyrochlore lattice, and $A^{2+}$ ions construct a non-frustrated diamond lattice. ZnCr$_2$O$_4$ and MgCr$_2$O$_4$ with nonmagnetic Zn$^{2+}$ and Mg$^{2+}$ exhibit molecular spin fluctuations [1-3] and excitations [4]. CoCr$_2$O$_4$ and MnCr$_2$O$_4$ with magnetic Co$^{2+}$ ($S = 3/2$) and Mn$^{2+}$ ($S = 5/2$) exhibit both ferromagnetic and ferroelectric polarizations called multiferroics, induced by conical spin structures [5; 6]. The spiral components rapidly grow below $T_S = 25$ K and 14 K, but cannot form long-range order because of the geometrical frustration among the Cr sites, whereas the axial ferrimagnetic components form long-range order by non-frustrated $A$-Cr interactions below $T_C = 93$ K and 51 K [7-9].

Recently, a further frustration effect on the spiral correlation was discovered in lowest temperature phases in the solid solution materials Co$_{1-x}$Zn$_x$Cr$_2$O$_4$ by neutron scattering and magnetic susceptibility measurements [10]. As $x$ increases from 0, the ferrimagnetic component disappears at $x \sim 0.35$, the remaining spiral clusters interestingly become not only small in size but also anisotropic in shape, and antiferromagnetic order with multiple propagation vectors appears above $x \sim 0.95$ [10]. However, no quantitative information of the anisotropic spiral clusters was given owing to lack of a large single crystal.

In this paper, we study the anisotropic spiral clusters using Mn$_{1-x}$Mg$_x$Cr$_2$O$_4$, of which large single crystals are available above $x \sim 0.9$ by our current technique. The spin system is also expected to be almost the same as in Co$_{1-x}$Zn$_x$Cr$_2$O$_4$. First, an unreported $x$-$T$ magnetic phase diagram is presented with polycrystalline magnetic susceptibility data. Next, single-crystalline neutron scattering data measured on Mn$_{0.07}$Mg$_{0.93}$Cr$_2$O$_4$ are given. Then, the anisotropic spiral clusters are semi-quantitatively discussed.
2. Experiments

Polycrystalline samples of Mn$_{1-x}$Mg$_x$Cr$_2$O$_4$ were synthesized by a solid-state reaction method in air from mixture of MnO, MgO and Cr$_2$O$_3$. All the samples were confirmed to be a single phase of a spinel structure by x-ray diffraction at room temperature. A single-crystalline sample of Mn$_{0.07}$Mg$_{0.93}$Cr$_2$O$_4$ with 4.4 mm diameter and 27 mm long was grown by a floating zone method under 6 atm Ar atmosphere.

Magnetic susceptibility was measured by a superconducting quantum interference device magnetometer (SQUID: Quantum Design MPMS-5). Neutron scattering was carried out on triple-axis spectrometers AKANE and TOPAN, installed at the thermal guide tube at JRR-3 and at the thermal beam hall of the same reactor in Japan Atomic Energy Agency (JAEA), Tokai, Japan, respectively. On AKANE, the incident energy was fixed at $E_i = 19.4$ meV with horizontal collimation sequence of guide-60'-60'-blank. On TOPAN, the final energy was fixed at $E_f = 14.7$ meV with horizontal collimation sequence of blank-100'-100'-blank. Each sample was enclosed with He exchange gas in an aluminum container, which was placed under the cold head of a closed-cycle He refrigerator.

3. Results

Figures 1(a) and 1(b) show the zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data measured on the polycrystalline samples with several compositions. Both $T_C$ and $T_S$ are observed in Fig. 1(a), and only $T_S$ is observed in Fig. 1(b). The two curves do not trace each other below $T_S$. Figure 1(c) shows the resultant phase diagram obtained from the anomaly temperatures.

As $x$ increases from 0, $T_C$ rapidly decreases and disappears at $x \approx 0.35$. The value of $T_S$ slowly decreases towards 9 K at $x = 0.90$ and increases again above $x = 0.90$. All the features are almost the same as in Co$_{1-x}$Zn$_x$Cr$_2$O$_4$ [10].

Figure 1. (Color online) (a)(b) Temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility measured on polycrystalline Mn$_{1-x}$Mg$_x$Cr$_2$O$_4$ under a magnetic field of $H = 200$ Oe. (c) Magnetic phase diagram of Mn$_{1-x}$Mg$_x$Cr$_2$O$_4$ obtained from the susceptibility data. The solid lines connect the experimental plots, and the dotted lines are guide for eyes.

Figure 2(a) shows the elastic neutron scattering intensity distribution in the $hk0$ zone measured at 4 K (< $T_f = 11$ K) on the single-crystalline sample Mn$_{0.97}$Mg$_{0.93}$Cr$_2$O$_4$. Very diffusive and anisotropic magnetic satellite reflections were observed around $(1.32, 1.32, 0)$, $(2.68, 1.32, 0)$ and $(1.32, 2.68, 0)$, which are described by the magnetic propagation vectors $Q_s = (-0.68, -0.68, 0)$, $(0.68, -0.68, 0)$ and $(-0.68, 0.68, 0)$ measured from $(2, 2, 0)$, respectively. The ratio of the peak intensity at $(1.32, 1.32, 0)$ to those at $(2.68, 1.32, 0)$ is estimated to be about 4.0(3). The diffuse scattering profile is well fitted by a Lorentzian like in MnCr$_2$O$_4$ [7] both along parallel and perpendicular to each $Q_s$. The full width at half maximum (FWHM) is estimated to be about 0.22 Å$^{-1}$ along $Q_s$ and about 0.63 Å$^{-1}$ perpendicular to $Q_s$. 

Figure 2(a), 2(b), 2(c)
These values are much larger than the resolution limit 0.03 Å⁻¹, estimated from the nuclear Bragg reflection (2, 2, 0). Thus the real-space correlation lengths (FWHM) are estimated to be 12.7 Å and 4.4 Å, respectively, corresponding to about 4.3 and 1.5 times of Cr-Cr distance by using the value of 2.95 Å in MgCr₂O₄ [11].

Figure 2(b) shows the constant-\(Q\) scan data measured at 4 K at (1.25, 1.25, 0) as the representative point in the diffuse scattering. A quasielastic feature is observed, indicating that the spiral correlation dynamically fluctuates.

Figure 2(c) shows the temperature dependence of the peak intensity at \(Q = 1.5 \text{ Å}^{-1} \sim |(1.32, 1.32, 0)|\) measured on the polycrystalline Mn₀.₀₇Mg₀.₉₃Cr₂O₄. The magnetic scattering intensity gradually decreases and almost disappears at 90 K.

4. Discussion

We roughly estimated the rotational plane of the spiral correlation in Mn₀.₀₇Mg₀.₉₃Cr₂O₄ from the observed intensity ratio. The spiral order is described by

\[
\vec{m}_{j,k} = m_{j,k}^{(0)} \{ \hat{e}_x \cos(\vec{Q}_s \cdot \vec{r}_{j,k} + \gamma_j) + \hat{e}_y \sin(\vec{Q}_s \cdot \vec{r}_{j,k} + \gamma_j) \},
\]

where \( \vec{m} \) is the magnetic moment, \( j \) labels the magnetic sublattice from 1 to 6 (two Mn sites and four Cr sites) in the \( k \)th unitcell, \( m_{j,k}^{(0)} \) is magnitude of the moment, \( \vec{r}_{j,k} \) is the position, \( \vec{Q}_s \) is identical to the propagation vector, \( \hat{e}_x \) and \( \hat{e}_y \) are unit vectors defining the rotational plane, and \( \gamma_j \) is the relative phase angle in the plane [8]. Then the magnetic scattering intensity is represented by

\[
S(\vec{Q}) = C |F(\vec{Q})|^2 L(\vec{Q})(1 + \cos^2 \theta) \left| \sum_{j=1}^{6} \exp \{ i(\vec{G} \cdot \vec{r}_j + \gamma_j) \} \right|^2,
\]

where \( C \) is a constant, \( F \) is the magnetic form factor, for which we used the values in Ref. [12], \( L \) is the Lorentz factor, \( \theta \) is an angle between the scattering vector \( \vec{Q} \) and the normal vector of the rotational plane, and \( \vec{G} \) is the reciprocal lattice vector corresponding to (2, 2, 0) in the present estimation [8]. Here we ignore the 7% Mn spins as the first approximation and reduce the \( j \) range from 1 to 4. In
addition, the four Cr sites are resolved into two sublattices $B_1$ and $B_2$, as shown in Fig. 3, and the phase angles are assumed to be $\gamma_{B_1} = -\gamma_{B_2}$, which are the same as for CoCr$_2$O$_4$ and MnCr$_2$O$_4$ [7-9].

Table I summarizes the intensity ratios calculated for a proper-screw model and two cycloid-screw models: $ab$-plane cycloid (CoCr$_2$O$_4$ type), $Q_c$-plane cycloid (MnCr$_2$O$_4$ type) [7-9]. Among the three models the proper-screw type is closest to the observed ratio. Figure 3 depicts the spatial correlation of the clusters, taking into account the anisotropic correlation lengths as well.

The proper-screw formation suggests disappearance of the ferroelectricity observed in MnCr$_2$O$_4$ with inverted Dzyaloshinskii-Moriya interactions. The origin is unclear at this stage. Further researches of the $A$-site substituted system are needed to understand and control the spiral clusters.

**Table I.** Calculated and observed ratios of the peak intensity at (1.32, 1.32, 0) to that at (2.68, 1.32, 0). The CoCr$_2$O$_4$ and MnCr$_2$O$_4$ types mean $ab$-plane and $Q_c$-plane cycloid models.

| Model Type          | CoCr$_2$O$_4$ Type | MnCr$_2$O$_4$ Type | Observation |
|---------------------|--------------------|--------------------|-------------|
| Proper-screw type   | 4.0                | 2.2                | 2.0         | 4.0(3)     |

**Figure 3.** (Color online) (a) Spiral ordering models for magnetic scattering intensity calculation. (b) A schematic picture of the anisotropic spiral clusters in Mn$_{0.07}$Mg$_{0.93}$Cr$_2$O$_4$. The balls represent Cr sites. The thick red and thin green arrows represent the spins on the two sublattices $B_1$ and $B_2$.

5. Conclusions

We studied the spiral short-range correlations in Mn$_{0.07}$Mg$_{0.93}$Cr$_2$O$_4$ by single-crystalline neutron scattering. The anisotropic correlation lengths (FWHM) were estimated to be about 4.3 and 1.5 times of Cr-Cr distance along parallel and perpendicular to the propagation vector $Q$, respectively. The spatial spin correlation was suggested to be the proper-screw type rather than the cycloid one.

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