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Long Periodic Helimagnetic Ordering in CrM_3S_6 (M = Nb and Ta)

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Abstract. We report long periodic chiral helimagnetic orderings in ferromagnetic inorganic compounds CrM_3S_6 (M = Nb and Ta) with a chiral space group of $P6_322$. Magnetization in polycrystalline samples and high resolution powder neutron diffraction were measured. Our powder neutron diffraction measurements in CrM_3S_6 successfully separated nuclear and magnetic satellite peaks, having the period of hundreds of angstroms along the $c-$axis. Therefore, we propose that the magnetic ordering in ferromagnetic CrM_3S_6 is not ferromagnetic, but long periodic chiral helimagnetic ordering.

1. Introduction

Chirality concept is playing a very important role in different areas of the knowledge from applied science such as new materials, nano, spintronic and biosciences to very basic sciences such as particle physics and cosmology. Regarding new materials for spintronic purposes, it crucial to understand how to control the chirality in molecules, crystals and magnetic structures. Recently, the relationship between crystallographic and magnetic chirality has received attention, because the sense of a chiral helical spin structure depends on the right- or left-handed chiral crystal structure that allows a Dzyaloshinskii-Moriya (DM) interaction [1, 2, 3, 4, 5]. When a magnetic field is applied perpendicular to the helical axis, the chiral helimagnetic structure continuously transforms into chiral magnetic soliton lattice in which the period is controlled by the field continuously [6]. Formation of the chiral magnetic soliton lattice is theoretically expected to exhibit attracting new phenomena [7, 8, 9, 10, 11]. In ferromagnetic-based chiral magnetic compounds, it can be shown that a cusp appears at the ordering temperature in the magnetization curves, which is an evidence of the chiral magnetic orderings [12]. However, the

pitch angle of the chiral helimagnetic ordering, mainly determined by the ratio of exchange interaction and DM interaction (D/J), is usually very small and the helimagnetic period can be hundreds of angstroms. In some cases, the angular resolution of conventional thermal neutron diffractometers is not high enough to separate fundamental Bragg and magnetic satellite peaks. As a consequence, some compounds with helimagnetic ordering may be easily misinterpreted as collinear ferromagnets.

TM_3S_6 (T = transition metal, M = Nb and Ta), intercalated system of $2H - MS_2$, is described by the chiral space group $P6_322$ [13, 14, 15]. Magnetization measurements of TM_3S_6 show apparently a variety of magnetic behaviors; paramagnetism for $TiNb_3S_6$, VNb_3S_6, $TiTa_3S_6$ and VTa_3S_6, antiferromagnetism for $FeNb_3S_6$, $CoNb_3S_6$, $NiNb_3S_6$, $CoTa_3S_6$ and $NiTa_3S_6$, and ferromagnetism for $CrNb_3S_6$, $MnNb_3S_6$, $CrTa_3S_6$, $MnTa_3S_6$ and $FeTa_3S_6$ [16, 17, 18]. $CrNb_3S_6$ has been recently paid attention due to the observation of the chiral helimagnetism and chiral magnetic soliton lattice. In single crystalline magnetization samples of $CrNb_3S_6$ and $MnNb_3S_6$, the magnetization shows a cusp around the magnetic transition temperature T_C, indicating formation of the chiral helimagnetism and chiral magnetic soliton lattice along the $c-$axis [19]. These incommensurate magnetic structures were directly probed by Lorentz transmission electron microscopy (TEM) [20]. Thermal neutron diffraction studies firstly reported that $CrNb_3S_6$ formed a ferromagnetic structure because the magnetic scattering peaks were observed at the same diffraction angle with nuclear ones [15]. However, small angle neutron scattering experiments probed a magnetic satellite peak with the period of 480 Å[21, 22]. Therefore, some of the apparently ferromagnetic TM_3S_6 compounds can be in fact chiral magnetic compounds forming incommensurate chiral magnetic structures with very long period.

In this paper, we demonstrate that high resolution powder neutron diffraction experiments make it possible to detect incommensurate satellite peaks with the period of hundreds of Å. We report magnetization and powder neutron diffraction experiments in $CrNb_3S_6$ and $CrTa_3S_6$. Our obtained results indicate that these compounds form long periodic incommensurate magnetic structures.

2. Sample preparation

The polycrystalline sample was prepared by the mixture of Cr, M (M = Nb or Ta) and S in the stoichiometric composition in an evacuated silica tube at 1000 °C for one week. The obtained samples were evaluated by X-ray powder diffraction using Cu $K\alpha$ radiation (Multiflex, Rigaku Co.). All the diffraction peaks were successfully indexed using the reported TM_3S_6 structure [13, 14, 15]. The lattice parameters along the $c-$axis were 12.076 Åand 12.126 Å for $CrNb_3S_6$ and $CrTa_3S_6$, respectively. Therefore, all the synthesized samples had no impurity phases.

3. Magnetization measurements

The polycrystalline magnetization measurements were performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5). Temperature dependences of magnetization in $CrNb_3S_6$ and $CrTa_3S_6$ are shown in Figs. 1 (a) and (b), respectively. The obtained data indicate that all the compounds show ferromagnetic responses. The magnetic transition temperature T_C in $CrNb_3S_6$ was 130 K, which is several K higher than the reported results [19, 20, 22]. The T_C in $CrTa_3S_6$ was 150 K, which is 35 K higher than the reported results [17]. These increases of the T_C were due to smaller amount of defects in Cr sites, and the details will be discussed elsewhere.

4. Spallation powder neutron diffraction measurements

High resolution powder neutron diffraction experiments were performed at BL08 (SuperHRPD) in the Materials and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC). The measurements were performed on a low-angle detector bank

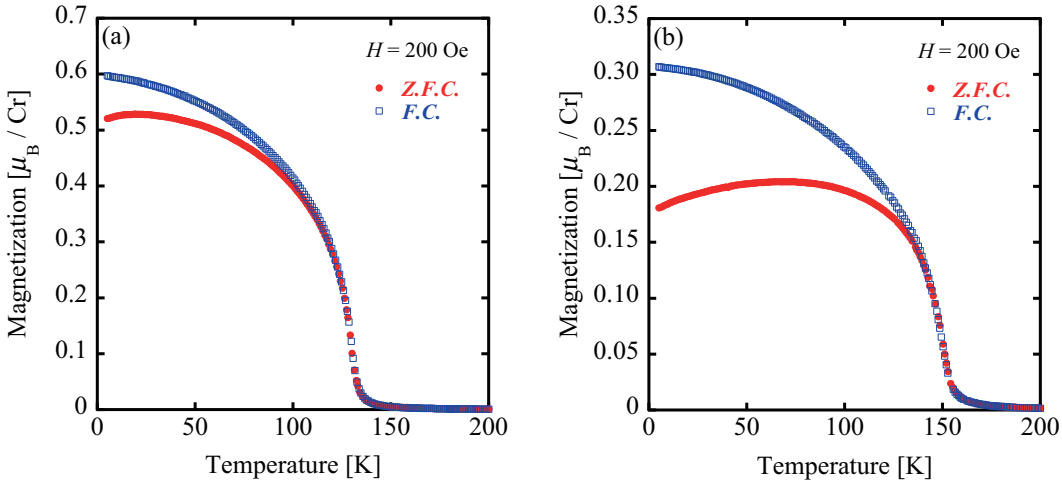

Figure 1. (color online) Temperature dependence of magnetization in (a) $CrNb_3S_6$, (b) $CrTa_3S_6$.

and a backward detector bank. The diffraction peaks were fitted by a pseudo-Voigt function, combining Gaussian and Lorentzian components. As evaluated by the nuclear (0,0,2) peak-width, q resolution of the backward detector bank was 3 times better than that of the low-angle detector bank. Powder diffractograms were collected at magnetic phase at 10 K and paramagnetic phase at 160 K and 180 K for $CrNb_3S_6$ and $CrTa_3S_6$, respectively.

Fig. 2 shows the results around the nuclear (0,0,4) and (1,0,3) reflections of $CrNb_3S_6$ and $CrTa_3S_6$ obtained by the backward detector bank. As indicated by the vertical arrows shown in Fig. 2 (a), we successfully separated the magnetic satellite peaks of $CrNb_3S_6$ around the (0,0,4) and (1,0,3) reflections. All the observed satellite peaks were well indexed by the magnetic propagation vector $k_{mag} = (0, 0, \delta)$ with $\delta = 0.021$. The determined helimagnetic period was slightly longer than the reported value [20, 22]. The fewer defects in Cr sites due to larger T_C may change the helical periodicity governed by D/J. While the thermal powder neutron diffraction measurements of $CrTa_3S_6$ have been reported to be ferromagnetic structure [15], our obtained data shown in Fig. 2 (b) clearly separated the nuclear peaks and magnetic satellite peaks, indicating a helimagnetic structure with the period of 225 Å. We also observed the magnetic satellite peaks around the (0,0,2) reflection on the low-angle detector bank. All the observed satellite peaks were well indexed by the magnetic propagation vector $k_{mag} = (0, 0, \delta)$ with $\delta = 0.054$.

5. Conclusion

In this paper, we succeeded in detecting incommensurate magnetic ordering with the period of hundreds of angstroms in CrM_3S_6 (M = Nb and Ta). While the magnetization measurements of $CrNb_3S_6$ were consistent with the reported results, the magnetic transition temperature T_C of $CrTa_3S_6$ was 35 K higher than that of the reported results[17]. The high resolution powder neutron diffraction of $CrNb_3S_6$ and $CrTa_3S_6$ separated fundamental nuclear Bragg peaks and magnetic satellite peaks with the period of hundreds of angstroms. The magnetic satellite peaks were indexed with the magnetic propagation $k_{mag} = (0, 0, \delta)$, and δ for $CrNb_3S_6$ and $CrTa_3S_6$ were 0.021 and 0.054, respectively. As the crystal structure of CrM_3S_6 is chiral, the observed magnetic satellite peaks in $CrTa_3S_6$ indicate formation of long periodic chiral helimagnetic ordering due to DM interaction.

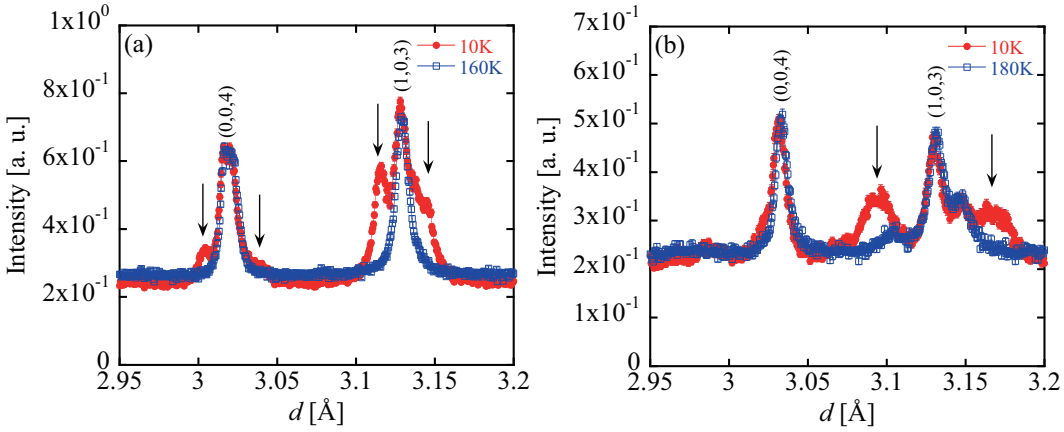

Figure 2. (color online) Neutron powder diffractograms around the nuclear (1,0,3) and (0,0,4) reflections in (a) $CrNb_3S_6$ and (b) $CrTa_3S_6$. The vertical arrows indicate observed magnetic satellite peaks indexed by $k_{mag} = (0, 0, \delta)$ ($\delta = 0.021$ for $CrNb_3S_6$ and 0.054 for $CrTa_3S_6$).

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