

## Neutron powder diffraction study on new square-lattice antiferromagnets $\text{Sr}_2\text{CrO}_3\text{X}$ ( $\text{X} = \text{F}$ and $\text{Cl}$ )

Yoshihiro Tsujimoto, Shinichiro Asai, Maxim Avdeev, Takatsugu Masuda, Kazunari Yamaura  
*NIMS, ISSP, ANSTO*

Development of the understanding of the transition metal oxides has triggered the search for hetero-anion containing metal oxides because incorporation of hetero anions which possess different charge, electronegativity, and ionic size from the oxide ion opens up possibilities for inducing new physical and chemical properties that the corresponding pure oxide does not exhibit. Recently, we have demonstrated that controlling mixed-anion site ordered patterns is a new effective approach to drastically switch the magnetic/electronic ground states [1]. For example,  $\text{Sr}_2\text{NiO}_3\text{X}$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ) with the low spin state ( $S = 1/2$ ) adopts the  $\text{K}_2\text{NiF}_4$  type structure, but the nickel cation takes a square pyramidal coordination with apical  $\text{O}/\text{X}$  anions being ordered for  $\text{X} = \text{Cl}$  and disordered for  $\text{F}$  (Fig. 1a). Each square pyramid  $\text{NiO}_5$  is linked by corner sharing so as to form a two-dimensional square lattice. In contrast to related layered compounds such as  $\text{K}_2\text{NiF}_4$  and  $\text{La}_2\text{CuO}_4$  having the strong superexchange interactions through  $d_{x^2-y^2}$  and  $\text{O}2p$  orbitals, the half-filled  $d_{xy}$  orbital in  $\text{Sr}_2\text{NiO}_3\text{X}$  gives rise to sizable direct (FM) interactions along the diagonal direction on a square, the magnitude of which depends on the direction of Ni-centered square pyramids (or the  $\text{O}/\text{X}$  site ordered patterns). As a result,  $\text{X} = \text{Cl}$  undergoes an AFM ordering at  $T_N = 47$  K, and a spin disordered state below 11 K for  $\text{X} = \text{F}$ .

In order to develop our approach, we synthesized new chromium oxyhalide compounds,  $\text{Sr}_2\text{CrO}_3\text{X}$  ( $\text{X} = \text{F}$ ,  $\text{Cl}$ ) with  $(t_2g)^3$  orbitals, by high-pressure method, which are isostructural with  $\text{Sr}_2\text{NiO}_3\text{X}$  including the  $\text{O}/\text{X}$  ordered patterns. As we expected, the chromium oxyhalides exhibit greatly different magnetic susceptibility curves be-

tween them.  $\text{X} = \text{F}$  and  $\text{Cl}$  show a broad maximum at  $T_{\text{max}} = 290$  and  $56$  K, respectively. The magnetic phase transition temperatures, which are estimated from  $dX/dT$ , are  $150$  K for  $\text{X} = \text{F}$  and  $27$  K for  $\text{X} = \text{Cl}$ . In this study, we conducted neutron powder diffraction experiments using ECHIDNA instrument installed in ANSTO to investigate their magnetic ground state. Figure 1c shows the temperature evolution of the neutron diffraction patterns collected from the oxyfluoride. At the base temperature, some addition peaks which could not be assigned by the chemical unit cell were clearly observed. These peaks disappeared above  $150$  K, and thus the origin of them should be magnetic. Rietveld refinement gave the best agreement with the propagation vector  $k = (1/2 \ 1/2 \ 0)$  and Cr spins aligned along the  $c$  direction. The figure 1d displays the temperature variation of the magnetic moments. They increase with decreasing temperature and the magnitude of them is approximately  $2.0 \mu_B$  at  $3$  K. This is consistent with the trivalent chromium ion. In contrast, the neutron diffraction pattern for  $\text{Sr}_2\text{CrO}_3\text{Cl}$  evidenced no long-range magnetic order down to  $3$  K (Fig 1b). The data showed only two magnetic peaks which could be assigned to  $(1/2 \ 1/2 \ 0)$  and  $(1/2 \ 1/2 \ 1)$ . No observation of  $(1/2 \ 1/2 \ 1)$ ,  $l > 1$  suggests that Cr spins are antiferromagnetically correlated in a bilayer unit, but a magnetic correlation between bilayers are negligible. It is very interesting to clarify what makes the difference in the magnetic ground states of the oxychloride and oxyfluoride.

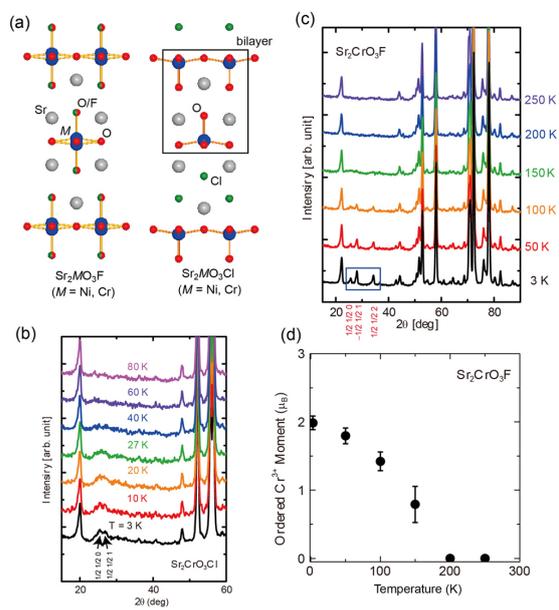


Fig. 1. Fig. 1(a) Crystal structures of  $\text{Sr}_2\text{MO}_3\text{X}$  ( $M = \text{Ni, Cr}$ ;  $\text{X} = \text{F, Cl}$ ). (b, c) Neutron diffraction patterns collected from  $\text{Sr}_2\text{CrO}_3\text{Cl}$  and  $\text{Sr}_2\text{CrO}_3\text{F}$  at various temperatures. (d) Temperature evolution of the magnetic moments of  $\text{Cr}^{3+}$  spin in  $\text{Sr}_2\text{CrO}_3\text{F}$ .