MAGNETIC PHASE TRANSITION IN
Mn$_3$ZnC PEROVSKITE
PROBED BY Mn K-EDGE

Magnetic phase transitions in itinerant-electron systems have currently attracted basic interest in magnetism. In such systems, metallic perovskites Mn$_3$MX ($M = Al, Zn, Ga, Sn$, etc., $X = C$ and $N$) show various prominent features associated with the transitions, e.g., metamagnetism, pressure dependence, magneto-volume effect, etc., and the electronic states of Mn atom have received extensive interest. Here, we choose the Mn$_3$ZnC perovskite, a typical compound with a second-order phase transition [1]. The sample Mn$_3$ZnC was supplied by Dr. D. Fruchart of CNRS, Grenoble. As temperature is decreased, Mn$_3$ZnC undergoes the transition from ferromagnetism to ferrimagnetism at $T_t = 233$ K with a tetragonal distortion. In the ferrimagnetic phase, the magnetic unit-cell consists of 12 Mn atoms occupying three different crystallographic sites, forming a non-collinear structure composed of two canted-ferromagnetic layers – Mn(I) and Mn(II) – and two uniaxial ferromagnetic layers – Mn(III) (Fig. 1). Correlation between the appearance of the non-collinear spin structure and the magnetic states of Mn atoms is very intriguing problem in the itinerant systems. However, there has been no spectroscopic study on Mn atoms in Mn$_3$MC perovskite systems. Temperature variation of X-ray magnetic circular dichroism (XMCD) at the Mn K-edge is suitable for studying the phase transition from the viewpoint of the Mn electronic states. Although the K-edge XMCD generally shows a very weak signal and a complicated profile, helicity-modulation (HM) technique can greatly improve the statistical accuracy and resolution of XMCD spectrum [2].

In this work we used Mn$_3$ZnC powder. The phase transition was confirmed by magnetization measurement under a fixed magnetic field of 0.6 T, and the critical temperature was determined. The XMCD spectra were recorded in the transmission mode by the HM method under the same strength of 0.6 T. Temperature variation was measured with high precision around the phase transition point. Absorption-edge energy $E_0$ was determined as the first inflection point of XANES spectrum.
Figure 2 shows the XANES and XMCD spectra in the ferromagnetic phase at $T = 300$ K. A remarkable dichroic spectrum is observed in a narrow range around the edge. It is characterized by the dispersion-type spectrum having a positive peak just on the edge and a negative one at 3 eV higher than the edge. This is very similar to the Fe K-edge XMCD in ferromagnetic Fe compounds, which suggests that the Mn 3$d$ states in the carbide resemble the electronic structure of Fe atoms. Temperature variation of the Mn K-edge XMCD spectrum is demonstrated in Fig. 3 by a three-dimensional drawing reconstructed from the serial data. The spectrum shows a rapid variation with temperature. As the temperature is decreased, the positive peak intensity increases first monotonically and then rapidly after crossing the transition temperature, while the negative peak is gradually reduced in its amplitude and remains negative over the temperature range measured. Hence, we find that the spectrum shows a growing positive contribution with decreasing temperature. This trend is clearly shown in Fig. 4, in which the temperature variation of the magnetization forms a cusp at $T_t = 233$ K due to the second-order phase transition. As the temperature is decreased further, the integrated intensity changes the sign from negative to positive at about 180 K; i.e., the positive contribution overcomes the negative component at lower temperatures. This behavior is explained as follows: the observed spectrum is an averaged effect of the three Mn sites, and the negative
intensity originates in the ferromagnetic phase, so that the deviation is ascribed to appearance of the canted-ferromagnetic layers in the ferrimagnetic phase.

What does the peculiar temperature variation of the XMCD intensity imply? According to the K-edge sum rule [3], the integrated intensity could be connected with the expectation value of orbital angular momentum per Mn 4p hole. Therefore, the present results indicate that the orbital moment of the 4p bands is not quenched and changes its sign from positive to negative when the temperature decreased. It is generally accepted that 4p bands polarization mainly results from 3d – 4p hybridization via neighboring atoms. The hybridization through the 2p orbitals of C ligands may play a crucial role for the canted-spin structure. The evolution of XMCD spectrum probably reflects an abrupt change in the density of states at the Fermi level, which occurs in the Mn e_g orbitals located at the top of the 3d bands.

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References

Fig. 4. Temperature dependence of the Mn K-edge XMCD integrated intensity, which is compared with temperature variation of magnetization. An abrupt deviation happens almost simultaneously at the transition temperature.