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Structural transition of spinel compound $NiCr_2O_4$ at ferrimagnetic transition temperature

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Abstract

Magnetic properties and crystal structure of spinel compound $NiCr_2O_4$ have been investigated by magnetization and high-resolution X-ray powder diffraction measurements. The structural transition from tetragonal to orthorhombic symmetry was observed at ferrimagnetic transition temperature. This crystal distortion is related to the magnetic ordering of ferrimagnetic component.

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Keywords: Spinel compound; Ferrimagnetic ordering; Structural transition; X-ray diffraction

Spinel compound $NiCr_2O_4$ exhibits a ferrimagnetic ordering below $T_C = 74$ K. Recently, another magnetic transition at $T_S = 31$ K was found by Tomiyasu et al. [1], i.e., only the ferrimagnetic component shows an ordering at T_C and the ordering of the antiferromagnetic component is followed below T_S. A unique magnetic structure model below T_S was proposed from neutron diffraction and magnetization measurements [1], which is different from a spiral ordering usually observed in spinel chromites such as $CoCr_2O_4$ and $MnCr_2O_4$. On the other hand, $NiCr_2O_4$ with a normal spinel structure shows a structural transition from cubic to tetragonal symmetry at ~310 K due to a Jahn–Teller effect on Ni^{2+} ions at a tetrahedral site. Further, another structural transition was found at 65 K [2], which is slightly different from the magnetic transition temperature. However, the correlation between magnetic and structural properties has not been investigated so far. In the present study, the details of the magnetic properties and the crystal structure of $NiCr_2O_4$ were investigated by magnetization and high-resolution X-ray powder diffraction measurements.

$NiCr_2O_4$ sample was prepared by heating the mixture of high purity NiO and Cr_2O_3 in air. Temperature dependence of magnetization was measured by SQUID magnetometer. High-resolution X-ray powder diffraction experiments using synchrotron radiation were performed at a beam line of BL-3A at the Photon Factory, KEK in Tsukuba, Japan. A wavelength of incident beam used was 1.600 Å. A flat Si(1 1 1) crystal analyzer was used in order to improve the angular resolution. The temperature dependence of the diffraction profiles of specific reflections were measured at temperatures between 12 and 100 K.

The temperature dependence of magnetization of $NiCr_2O_4$ under a magnetic field of 100 Oe is shown in Fig. 1(a). There are two magnetic transition at $T_C \approx 75$ K and $T_S \approx 30$ K, which are fairly good agreement with reported one [1]. Fig. 1(b) shows the inverse of magnetic susceptibility χ^{-1}. Above T_C, the $T - \chi^{-1}$ curve is nearly represented by a hyperbola, therefore it is found that $NiCr_2O_4$ indicates a ferrimagnetic behavior below T_C.

Fig. 2 shows the temperature dependence of powder diffraction profiles of 004_t and 400_t reflections, where the indices of Bragg reflections are based on a tetragonal cell with the lattice constants of a~8.18 and c~8.55 Å. Above ~70 K, 400 reflection in a cubic phase splits into two peaks of 400_t and 004_t reflections due to a tetragonal distortion. However, the peak profile of 400_t reflection becomes broader with decreasing temperature below ~60 K and clearly splits into two peaks at the lower temperatures. This

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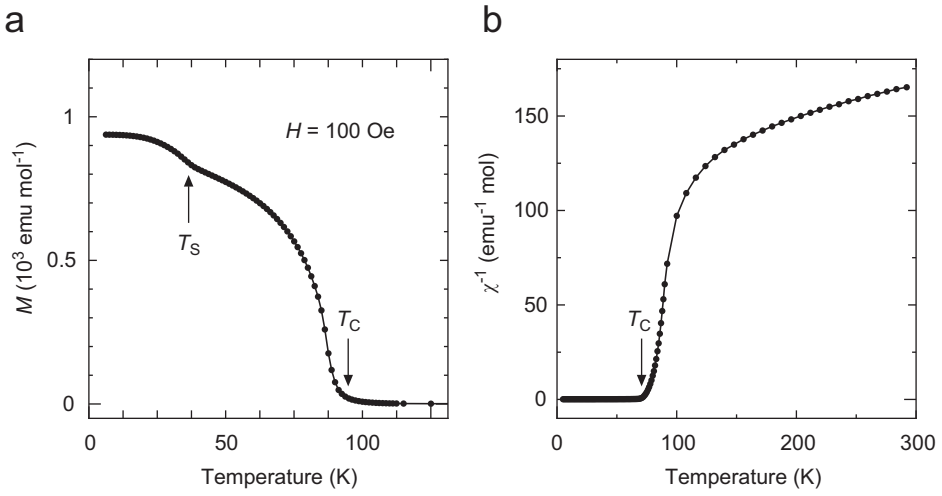

Fig. 1. Temperature dependence of (a) magnetization and (b) inverse susceptibility $\chi^{-1} = (M/H)^{-1}$ of $NiCr_2O_4$.

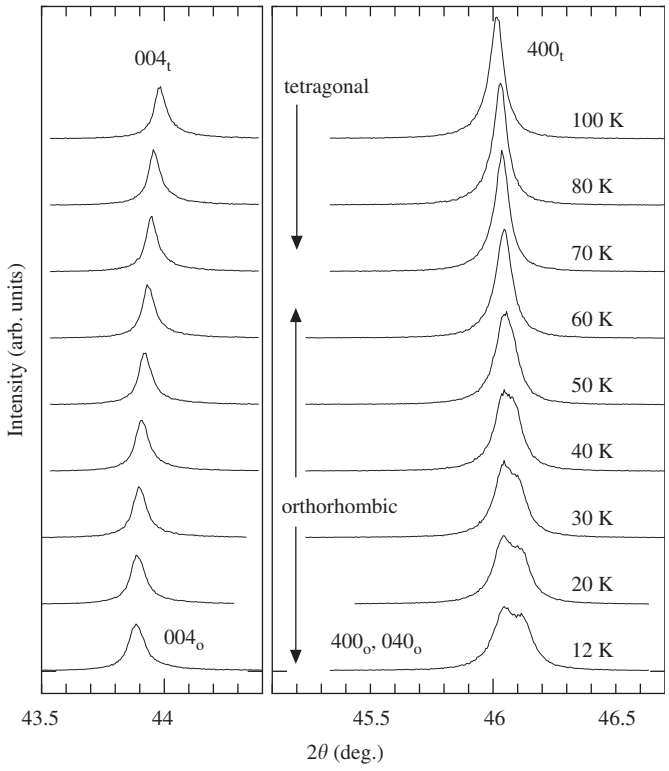

Fig. 2. Temperature dependence of X-ray diffraction patterns of 004_t and 400_t reflections of $NiCr_2O_4$.

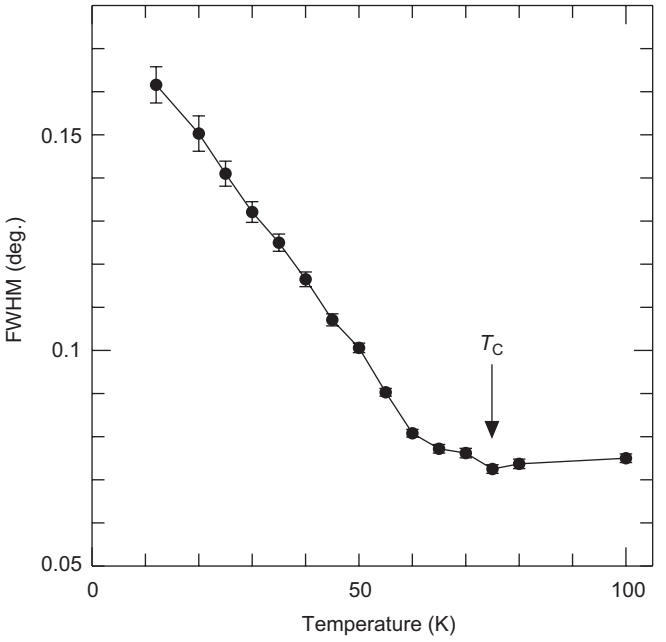

Fig. 3. Temperature dependence of full width at half maximum (FWHM) of 400_t reflection.

means that the structural transition occurs at 60−70 K. In order to clarify the structural transition temperature T_t, the line widths of 400_t reflection were determined by a profile fitting method. The temperature dependence of the full width at half maximum (FWHM) of 400_t reflection is shown in Fig. 3. The FWHM increases gradually with decreasing temperature below ~65 K. Thus T_t seems to be about 65 K, which is lower than T_C. However, a single phase transition at about 70 K was observed by the heat capacity measurement [3], therefore it is plausible that the structural transition and magnetic one occur simultaneously. The discrepancy between the observed T_t and T_C can be reasonably explained by the followings: (i) The lattice distortion may be too small to be observed just below T_C, where the magnitude of magnetization is small. (ii) When the powder sample is exposed by strong synchrotron radiation, the actual temperature of the sample becomes somewhat higher than that indicated by a sensor, sometimes up to 10 K even if the sensor is set near the sample. Therefore, it is concluded that the true T_t is the same as T_C within an experimental error.

Next, we carefully checked the peak splitting for the other reflections. It is found that the crystal symmetry of $NiCr_2O_4$ below T_C is orthorhombic. In this case, the lattice constants a, b and c can be calculated from the peak

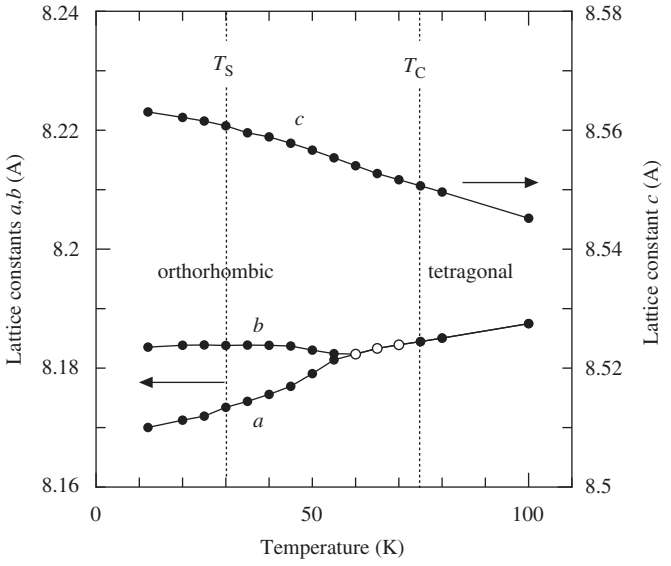

Fig. 4. Temperature dependence of lattice constants of $NiCr_2O_4$. Open circles indicate the lattice constant on the assumption that the peak position of 040_o is the same as that of 400_o.

positions of 400_o, 040_o and 004_o reflections, respectively, where indices are based on an orthorhombic cell. We determined the peak position for each reflection using a profile fitting technique. It is noted that the peak position of 400_o and 040_o reflections just below T_C is too close to decompose them into two peaks, therefore the tetragonal structure was assumed between 60 and 70 K even below T_C. Fig. 4 shows the temperature dependence of the lattice constants thus obtained. c decreases monotonously with decreasing temperature and shows no anomaly at both T_C and T_S. While, a and b separates gradually with decreasing temperature below T_C, thus the structural transition at T_C seems to be of second order, which is consistent with the fact that the structural transition is correlated with magnetic one. On the other hand, it is found that a, b and c indicate no evident anomaly at T_S.

According to the magnetic structure model of $NiCr_2O_4$, spontaneous magnetization is along [1 0 0] or [0 1 0] direction below T_C [1]. In our result, the structural transition at T_C induces the distortion along a or b, therefore the orthorhombic distortion seems to be strongly coupled with the ferrimagnetic component. On the other hand, no structural anomaly at T_S implies that the ordering of the antiferromagnetic component does not affect a long range ordering of the crystal distortion. More detailed crystal structure analysis for the ferrimagnetic phase is now in progress to determine the atomic distances and the bond angles and to discuss the magnetic interaction and the origin of the unique magnetic structure in $NiCr_2O_4$.

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