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MÖSSBAUER STUDY OF SPIN STRUCTURAL BEHAVIOR FROM THE INCOMMENSURATE TO THE COMMENSURATE STATES

Kang Ryong Choi¹, Seung-Iel Park¹, Sam Jin Kim¹, Chul Sung Kim¹

¹ Department of Physics, Kookmin University, Seoul 136-702, Korea

In order to elucidate the role of Cr ions in MCr₂O₄ exhibiting various magnetic properties[1,2], we have substituted a small amount of Fe ions for Cr sites and investigated the magnetic behavior of Fe ions, on nano scale, using Mössbauer measurement. The similar ionic radii of Fe²⁺ (0.64 Å) and Cr³⁺ (0.63 Å) mean that lattice distortion effects of the substitution may be ignored. Here, we present crystallographic and magnetic properties of MCr₂⁻ₓFeₓO₄ (M= Ni, Zn) by using x-ray diffractomter (XRD), vibrating sample magnetometer (VSM), superconducting quantum interference device magnetometer (SQUID), and Mössbauer spectroscopy.

The spinel MCr₂⁻ₓFeₓO₄ (M= Ni, Zn) powders were prepared by wet chemical solution process. Weighted amounts of transition metal nitrate, chrome nitrate, and Fe isotope were dissolved in acetic acid, ethanol, nitric acid, and distilled water. The solution was refluxed at 80 °C for 12 hours to allow the gel formation and then dried at 120 °C in a dry oven for 24 hours. The dried powder was ground and annealed at 1000 °C for 3 hours in air.

The MCr₂⁻ₓFeₓO₄ (M= Ni, Zn) samples have a cubic normal spinel structure (Fd-3m) at room temperature. Figure 1 shows the X-ray diffraction pattern of Rietveld refinement for ZnCr₂⁻ₓFeₓO₄. The lattice constants a₀ were determined to be 8.318 ~ 8.340 Å, respectively.

Mössbauer spectra of MCr₂⁻ₓFeₓO₄ (M= Ni, Zn) were taken from 4.2 to 295 K using a ⁵⁷Co source in a rhodium matrix. Figure 2 shows the representative Mössbauer spectra for Zn Cr₁.₉₈⁵⁷Fe₀.₀₂O₄. The Neel temperatures for NiCr₁.₉₈⁵⁷Fe₀.₀₂O₄ and Zn Cr₁.₉₈⁵⁷Fe₀.₀₂O₄ are determined to be 90 K and 12.5 K, respectively. We conclude that the lower Neel temperature in ZnCr₁.₉₈⁵⁷Fe₀.₀₂O₄ is interpreted in terms of B-B exchange interaction.

The Mössbauer absorption spectra in all of chromites at 4.2K show that the well developed two sextets are superposed with small difference of hyperfine fields(Hₐ) caused by Cr³⁺ ions have two different magnetic sites. The values of the isomer shifts show that the states are in Fe³⁺ states for all temperature ranges. Ni-chromites Mössbauer spectra below the T_N show the line broadening with the Jahn-Teller distortion and accompanying relaxation effects, respectively. Zn-chromites Mössbauer spectra are observed that spin structural behavior of Cr ions is changed from the incommensurate to the commensurate states.


Figure 1. XRD patterns of ZnCr₁.₉₈⁵⁷Fe₀.₀₂O₄.

Figure 2. Mössbauer spectra of Zn Cr₁.₉₈⁵⁷Fe₀.₀₂O₄.