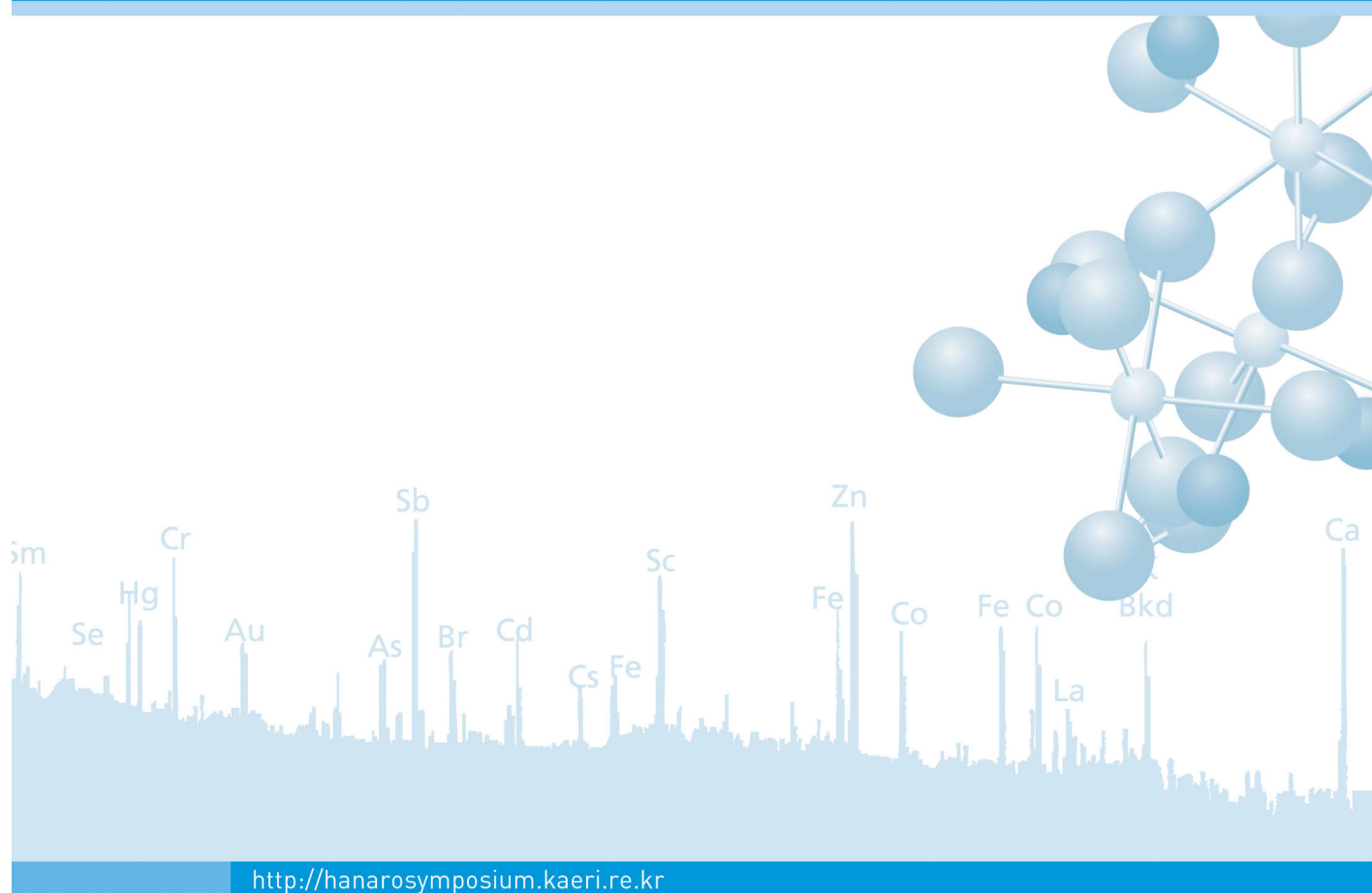


하나로심포지움 2006 HANARO SYMPOSIUM



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- 주관 : 과학기술부, 한국원자력연구소
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Magnetic properties of FeCr₂Se₄

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1. Introduction

Recently AB₂X₄ (A, B = transition metal, X = chalcogenide material) materials are reported for metal-to-insulator transition at high pressures, and also metallic and insulator spin-glass properties [1, 2]. Chalcogenide materials are studied for various crystallographic and magnetic properties according to doped transition material on tetrahedral site (A) and octahedral site (B). This is essentially related to the great flexibility of the structure in hosting various metal ions, with a possibility of reciprocal substitution between them [3]. Especially FeCr₂Se₄ has been reported to have a monoclinic unit cell and antiferromagnetic transition temperature is 218 K. This material has been studied both crystallographically and magnetically by several investigators. But different investigators have obtained different values for its cell dimensions and magnetic properties. Morris *et al.* reported that the magnetic susceptibility had maximum near 260 K [4]. On the other hand, Kojima *et al.* showed that the Néel temperature was 218 K [5]. Therefore it is necessary to disclose some unclear points and magnetic interaction mechanism on FeCr₂Se₄. Here, we present crystallographic and magnetic properties using the x-ray diffractometer (XRD), neutron diffraction, and Mössbauer spectroscopy for FeCr₂Se₄.

2. Experiment

Mixtures of the elements Fe, Cr, Se in the proper proportions were sealed on evacuated quartz ampoules and heated at 1000 °C for 72 h and then slowly cooled down to room temperature at a rate of 0.2 °C/min. The crystal structure of the sample was examined by x-ray diffractometer with CuK α radiation, and HRPD (High Resolution Powder Diffractometer, $\lambda = 1.8345$ Å) at HANARO reactor of the Korea Atomic Energy Research Institute. The Mössbauer spectra were recorded using a conventional spectrometer of the electromechanical type with a ⁵⁷Co source in a rhodium matrix.

3. Results and discussion

The crystal structure of FeCr₂Se₄ was solved from the XRD and neutron diffraction data at room temperature, by the Rietveld analysis. Fig.1 presents the observed and calculated peak profile, with Bragg positions of the XRD at room temperature. The crystal structure of the FeCr₂Se₄ is determined to be the monoclinic structure

*I*2/*m* (Fe (2a); Cr, Se (4i)) with its lattice constants $a = 6.26$ Å, $b = 3.61$ Å, $c = 11.78$ Å, and $\beta = 90.73^\circ$, respectively. These results are in agreement with the neutron diffraction results at room temperature.

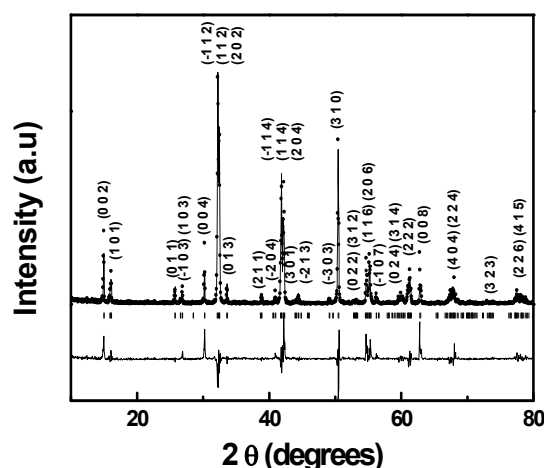


Fig. 1. XRD pattern for FeCr₂Se₄ at room temperature.

Fig.2 shows the neutron diffraction patterns of FeCr₂Se₄ from 4.2 to 295 K. Below the Néel temperature ($T_N = 220$ K), both the magnetic peaks and the crystal peaks were present together. Also, the magnetic superstructure peak of (1' 0' 3') reflection for magnetic unit cell $A \times B \times C (= 2a \times b \times 2c)$ develops rapidly with decreasing temperature. According to the result of neutron diffraction studies, the individual spin magnetic moments of the Fe and Cr ions are coupled antiferromagnetically along the C-axis with the distance of 2.956 Å, while they are coupled ferromagnetically along the B-axis with the distance of 3.617 Å with C-type ordering [6]. Namely, in a point of exchange interaction, each magnetic ion is coupled with antiferromagnetic interaction, and simultaneously, it participates in the ferromagnetic exchange interaction via neighbour magnetic ions. Since the strength of exchange interaction is inversely proportional to the ionic bond length, one can see that antiferromagnetic exchange interaction is stronger than ferromagnetic exchange interaction. This suggests that stronger antiferromagnetic exchange interaction covers the whole temperature range, while weaker ferromagnetic exchange interaction covers the low temperature range. In order to investigate the microscopic interaction mechanism between the magnetic hyperfine field and the quadrupole interaction, the Mössbauer spectra were

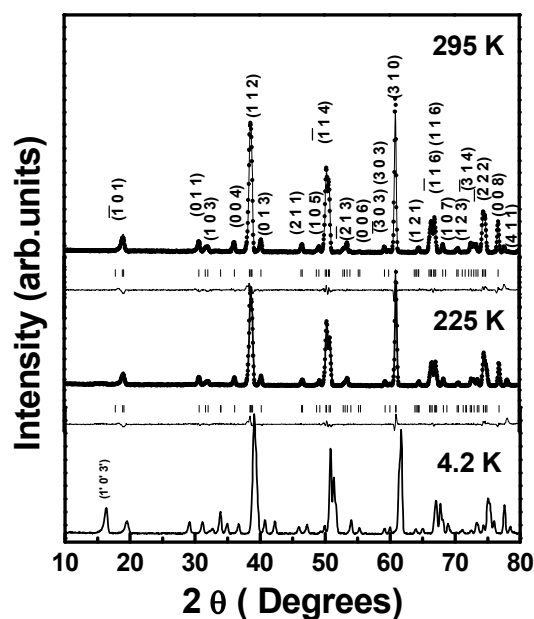


Fig. 2. Neutron diffraction patterns of FeCr_2Se_4 at temperature ranging from 4.2 to 295 K.

obtained. Mössbauer spectra at various temperatures ranging from 4.2 to 295 K are shown in Fig.2.

The Mössbauer spectrum shows a distorted line broadening at 4.2 K. Below T_N (220K), the doublet Mössbauer spectra split into several lines due to antiferromagnetic ordering. We have analysed the Mössbauer spectra using the full Hamiltonian for the ^{57}Fe nucleus considering both magnetic dipole and electric quadrupole interactions. These were analysed by diagonalizing a 4×4 magnetic hyperfine and quadrupole interaction matrix for the first excited state of ^{57}Fe and fitting eight Lorentzians to the calculated relative line positions and relative line intensities. Magnetic hyperfine field (H_{hf}) and quadrupole splitting (ΔE_Q) at 4.2 K have been fitted, yielding the following results: $H_{\text{hf}} = 108.8$ kOe, $\Delta E_Q = -1.65$ mm/s, and $R = -2.25$, where R is the ratio of electric quadrupole interaction to magnetic dipole interaction. It is noticeable that the absolute value of R is greater than 1 for all temperature range. It indicates that quadrupole interaction is larger than that of the magnetic dipole interaction. The spectrum above Néel temperature shows a doublet line, which means that the local symmetry around Fe ion in monoclinic lattice is distorted. The isomer shift δ at room temperature is 0.66 mm/s relative to Fe metal, which means that the charge state of Fe ions is ferrous in character.

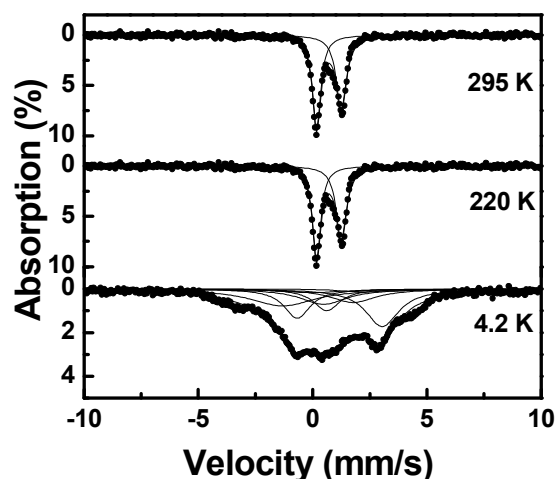


Fig. 3. Mössbauer spectra of FeCr_2Se_4 at various temperatures.

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