

## BD05

### Spin-Ordering Leading Magnetic Structure Transition in Sulphur System $A\text{Cr}_2\text{S}_4$ (A=Fe and Zn)

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Magnetic structure of  $\text{Fe}_{1-x}\text{Zn}_x\text{Cr}_2\text{S}_4$  ( $0 \leq x \leq 1$ ) has been studied with magnetic susceptibility, x-ray diffraction and Mössbauer spectra. The crystal structures are found to have a cubic spinel with space group  $Fd\bar{3}m$ . The lattice constants decrease with increasing Zn substitutions. According to magnetic susceptibility measurements, Néel temperature ( $T_N$ ) decreases with increasing Zn concentrations from  $x=0.5$  to  $0.7$ , specially  $T_N$  dramatically decreases from 105 K to 45 K. The magnetic ground state reveal transition from ferrimagnetic to anti-ferromagnetic behavior at  $x=0.7$ . It is interpreted that the order of magnetic ions between tetrahedral (A) site ion and octahedral (B) site ion is antiparallel. The Mössbauer spectra show asymmetrical shapes due to large electric quadrupole interaction, magnetic hyperfine field of samples decrease in ferrimagnetic behavior ranges and increase in antiferromagnetic behavior ranges at 4.2 K. The magnetic hyperfine field of all samples for Zn concentration  $x=0.0, 0.1, 0.3, 0.5, 0.7$  and  $0.9$  are 173, 156, 128, 116, 131 and 138 kOe, respectively. It is described that the magnetic dipole interaction was weakened as substituting Zn ions in replacement of Fe on A site.

## BD06

### Mössbauer Study of Two Discernable Fe Sites in $\text{CaFe}_2\text{O}_4$

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It is well known that a typical example of  $\text{AB}_2\text{O}_4$  oxide compounds is the spinel structure in which divalent and trivalent cations occupy, respectively, the octahedral and the tetrahedral sites of a cubic close packing of oxygen ions. Having the same compositional formula,  $\text{CaFe}_2\text{O}_4$  crystallizes entirely differently in the orthorhombic  $Pnma$  structure made up of distorted  $\text{FeO}_6$  octahedra sharing edges and corners, and 8-fold coordinated calcium atoms [1,2]. This study was carried out to clarify the structural aspects of  $\text{CaFe}_2\text{O}_4$  by means of Mossbauer spectroscopy.

Polycrystalline  $\text{CaFe}_2\text{O}_4$  was prepared by the solid state reaction method from high purity  $\text{CaCO}_3$  and  $\text{Fe}_2\text{O}_3$  powders. In order to get information about the crystal structure, Powder X-ray diffraction (XRD) pattern of the sample was analyzed by carrying out Rietveld profile refinement using the GSAS program. A Mössbauer spectrometer of a conventional transmission type was used with the constant acceleration mode over a temperature range from 4.2 K to 300 K. A  $^{57}\text{Co}$  source in a Rhodium matrix was used at room temperature.

Lattice parameters were  $a = 9.2373 \text{ \AA}$ ,  $b = 3.0237 \text{ \AA}$ ,  $c = 10.7124 \text{ \AA}$ , which were in good agreement with the values in other literature [3]. Results of structural refinement indicate, however, that there are two slightly different iron sites in the sample. Mössbauer spectra at 4.2 K show a hyperfine sextet with a hyperfine magnetic field and an isomer shift 47.3 T and 0.36 mm/s, respectively. Close look at the spectrum revealed that the line width of each spectral lines were not uniform. Line width for the first absorption line was much broader than that of sixth and this asymmetry gradually diminished until the temperature increased up to 100 K. This means that there might be a considerable difference in local symmetry for the Fe sites at low temperature, which is discernable by Mossbauer spectroscopy. Mössbauer spectra above  $T_N$  (~160 K) were doublets with equal intensities, while there were no quadrupole splittings within experimental error below  $T_N$ , indicating that the line broadening can take place due to the distribution of quadrupole splitting from random orientation of electric field gradient axes.

#### REFERENCES

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