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Neutron diffraction studies of the magnetic ordering in the spinel oxide system $Mg_xCo_{1-x}Cr_xFe_{2-x}O_4$

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Abstract

Neutron diffraction studies were performed on the spinel oxide system $Mg_xCo_{1-x}Cr_xFe_{2-x}O_4$ ($x = 0.0$, 0.25, 0.50, 0.75 and 1.0) as a function of temperature. Presence of magnetic long-range order at low temperatures was confirmed from the evolution of Bragg reflections with the decrease of temperature. Magnetic structural properties were determined from the Rietveld analysis of neutron diffraction data recorded in the temperature range 10–810 K. Sublattice and net magnetic moments for various compositions at various temperatures were found out from the analysis. The transition temperatures were also determined for all the compositions. A decreasing ferrimagnetic order with increasing substitution was revealed from the decreasing ordered sublattice moments. Huge diffuse signals around the 111 Bragg diffraction line were observed in the neutron patterns of the composition $x = 1.0$ below the Curie temperature indicating the existence of magnetic spin clusters. Hysteresis and low field dc magnetization measurements were done on the compositions $x = 0.75$ and 1.0. Thermo-magnetic irreversibility in the zero-field cooled and field cooled magnetization together with a shallow transition below Curie temperature was also observed. The various observations suggest a canted ferrimagnetic ordering in the composition range $x \leq 0.75$ and a semi-spin glass like behavior at $x = 1.0$. A super-paramagnetic behavior below the paramagnetic state is also suggestive from the observed features.

Keywords: Spinel oxides; Ferrite; Neutron diffraction; Ferrimagnetic; Magnetic order

1. Introduction

Compounds with spinel structure have attracted large attention due to its changing magnetic properties upon substitution of different nonmagnetic and magnetic ions. The general formula for the spinel type materials is AB_2O_4 and the structure consists of a cage of oxygen ions with two interstitial locations for the cations of tetrahedral (A) and octahedral (B) site symmetries. When the two sublattices (A and B) are occupied by the magnetic ions, the magnetic super-exchange interaction between the moments of the atoms in tetrahedral and octahedral sublattices (J_{AB}) is much larger than that between the moments of atoms in either tetrahedral sublattice (J_{AA}) or octahedral sublattice (J_{BB}) and their relative strengths are given by: $|J_{AB}| \gg |J_{BB}|J_{AA}|$. Thus the moments of one sublattice is aligned antiparallel to that of the other rendering ferrimagnetic ordering. This impels the moments within both the A and B sites to be parallel despite the antiferromagnetic exchange interactions among them. Thus the AA and BB bonds are unsatisfied and frustrated in undiluted spinels. Selective substitution of nonmagnetic or magnetic atoms can alter the strengths of the exchange integrals significantly giving rise to many interesting spin configurations in the spinel compounds. This fascinating feature stimulated extensive research on spinel compounds and quite a large variety of magnetic configurations and disordered states have been reported from various kinds of studies [1–18]. There have been few reports on the effect of substitution of Cr for Fe in the spinels $CoFe_2O_4$ and $MgFe_2O_4$ [16–18]. It was reported that the substitution of magnetic ion Cr^{3+} affected the magnetic properties markedly similar to that of non-magnetic substitution [16–19]. Simultaneous substitution of Mg^{2+} for Co^{2+} and Cr^{3+} for Fe^{3+} in $CoFeO_4$ may bring in more interesting magnetic properties

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since in this case the exchange forces get doubly affected due to the presence of Cr^{3+} as well as a nonmagnetic impurity Mg^{2+}. In order to have a deeper understanding of the magnetic properties of such spinels, it is essential to look into the change in magnetic ordering arising from the substitutions. Neutron diffraction is much more suitable to characterize such complex systems magnetically since it can provide clear evidence of the presence of magnetic long-range order (LRO) and short range order (SRO) and the magnitudes and orientation of the sublattice magnetic moments [5,10–13]. In view of that the quaternary spinel system $Mg_xCo_{1-x}Cr_xFe_{2-x}O_4$ ($x = 0.0$, 0.25, 0.50, 0.75 and 1.0) was chosen for neutron diffraction study as functions of composition as well as temperature to have a clear understanding of the magnetic ordering in such a doubly substituted system. Our cation distribution study on the system reported recently [20] showed that the B site has become highly inhomogeneous in respect of magnetic ion concentration due to the presence of three types of magnetic ions (Cr^{3+}, Fe^{3+} and Co^{2+}) differing in strength of their magnetic moments and at the same time by the presence of the majority of nonmagnetic Mg^{2+} ions. Shukla et al. [21] reported the structural and magnetic properties of the system $Mg_xCo_{1-x}FeCrO_4$ ($x = 0.0$, 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) based on X-ray diffraction, magnetization, ac susceptibility and Mössbauer spectroscopy analysis. The concentration of Mg in their system ranges between 0.0 and 0.6 in steps of 0.1 and they did not study the compositions with higher concentration of Mg whereas, in our system the concentration of nonmagnetic Mg is in the range 0.0–1.0 in steps of 0.25 covering both low and high dilution range. Furthermore, Fe/Cr ratio is constant in their system while it has been varied in our system together with the variation of Mg/Co ratio. Therefore, due to varying concentration of both Mg and Cr the ratio of all the four cations is different in all of our chosen compositions from those studied by them. Finally, their ac susceptibility and Mössbauer measurements results could not provide clear information about the magnetic ordering of the system. To our knowledge no neutron diffraction work on our selected compositions or any such compositions close to those has been reported. But as explained before neutron diffraction is essential for unambiguous characterization of the magnetic structure of such a system. We have also performed low field magnetization and hysteresis loop measurements on two extremely substituted compositions ($x = 0.75$ and 1.0) in order to have a more clear picture of the magnetic properties of these two highly substituted compositions.

2. Experimental

Five samples belonging to the spinel series $Mg_xCo_{1-x}Cr_xFe_{2-x}O_4$ with $x = 0.0$, 0.25, 0.50, 0.75 and 1.0 were synthesized in the solid state sintering method. The details of the preparation of samples have been reported elsewhere [20]. Neutron powder diffraction measurements on all the samples were performed at a number of temperatures in the range 10–810 K using the high resolution powder diffractometer (HRPD) located at the 1G beam port of JRR3 reactor of Japan Atomic Energy Agency (JAEA), Tokai, Japan. The detection system of HRPD consists of an array of 64 ^{3}He detectors with equal spacing of approximately 2.5° for recording of the diffracted neutron data. A neutron wavelength of 1.823 Å was used in the experiment from a Ge (331) monochromator oriented at a take-off angle of 89°. The data were recorded in the 2θ range 2.5–162.45° in step-width of 0.05°. A cold temperature instrument and a high temperature furnace were used for the low and high temperature measurements respectively. Approximately 5 g of powdered sample of each of the compositions was used for the neutron measurements. The samples were contained in the outer cylinder of a concentric cylindrical vanadium sample holder with 6 mm outer cylinder diameter and 4 mm inner cylinder diameter in order to minimize the absorption of neutrons by the samples. Hysteresis, zero-field-cooled (ZFC) and field cooled (FC) magnetization measurements were done on the samples $x = 0.75$ and 1.0 using a SQUID magnetometer of Advanced Science Research Center of JAEA. Hysteresis measurements were done at 10 K in the field range ±7.0 tesla. ZFC and FC magnetization measurements were done as a function of temperature under applied fields of 20, 100 and 500 Oe. For the sample $x = 1.0$ the measurements were done in the temperature range 10–400 K under all the three applied fields using a cryostat. However, for the sample $x = 0.75$, ZFC and FC measurements under 500 Oe were done in the temperature range 10–560 K and under 100 and 20 Oe in the range 317–560 K. Because, at 100 and 20 Oe irreversible behavior in magnetization arose well above the room temperature and the measurements could not be continued down to 10 K due to non-coincidence of the measured curves arising from transfer of sample from furnace to cryostat.

3. Results and discussion

In spinel structure, the crystallographic and magnetic unit cell being the same the contributions to the Bragg peaks from the nuclear and magnetic scattering occur at the same scattering angles (2θ). Therefore, evolution of the intensity of the Bragg peaks at low temperature is a manifestation of the evolution of magnetic Bragg intensity. Fig. 1(a) shows the comparison of the low and high temperature diffraction patterns for the sam-

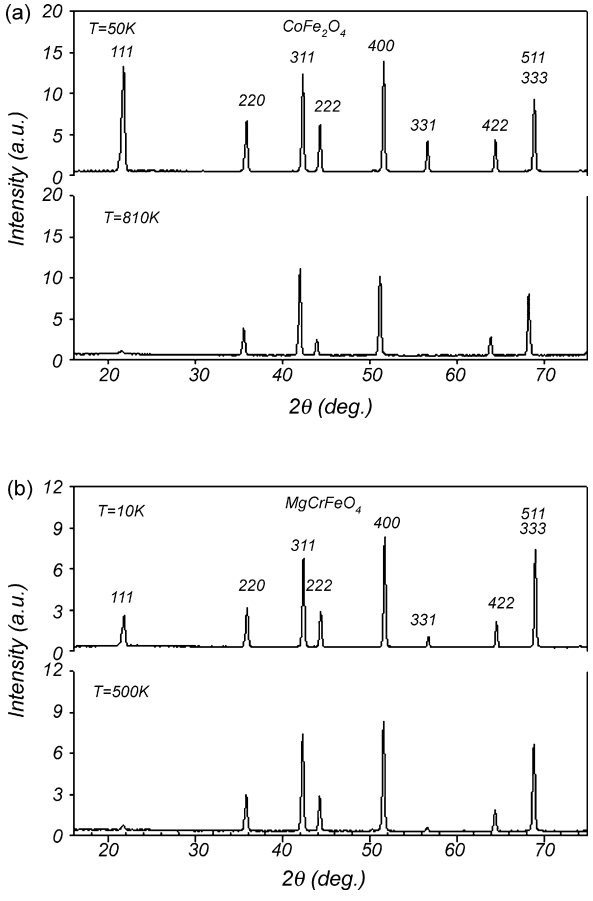

Fig. 1. Low-angle diffraction patterns of the samples (a) $x = 0.0$ and (b) $x = 1.0$ at different temperatures showing thermal evolution of the Bragg peaks.