ATOMIC MIGRATION IN MIXED FERRITE $Ni_xCo_{1-x}Fe_2O_4$

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The mixed ferrite $Ni_xCo_{1-x}Fe_2O_4$ have been investigated by X-ray and Mössbauer spectroscpy. From the results of X-ray diffraction measurement the structure for this system is spinel, and the lattice constant is in accord with Vegard's law. Mössbauer spectra of $Ni_xCo_{1-x}Fe_2O_4$ have been taken at various temperature ranging from 13 to 800 K. The isomer shifts indicate that the valence states of the irons at both A(tetrahedral) and B(octahedral) site are found to be in ferric high-spin states. The variation of magnetic hyperfine fields at the A and B sites are explained on the basis on A-B and B-B supertransferred hyperfine interactions. It is found that Debye temperatures for the A and B sites of $CoFe_2O_4$ and $NiFe_2O_4$ are found to be $\theta_A = 734 \pm 5$ K, $\theta_B = 248 \pm 5$ K and $\theta_A = 378 \pm 5$ K, $\theta_B = 357 \pm 5$ K, respectively. Atomic migration of $Ni_{0.3}Co_{0.7}Fe_2O_4$ starts near 450 K and increases rapidly with increasing temperature to such a degree that 61 % of the ferric ions at the A site have moved over to the B site by 700 K.

I. INTRODUCTION

Metallic atoms of a ferrimagnetic spinel are in an inverse distributions ; half the atoms of iron are in the tetrahedral(A) sites and the other half plus magnetic atoms in the octahedral(B) sites. However, $CoFe_2O_4$[1-2] is not completely inverse and the degree of inversion depends on the heat treatment. The area ratio, Fe(A)/Fe(B), has been found to vary from 0.61 ± 0.04 to 0.87 ± 0.04 for two extremes-quenched and slowly cooled $CoFe_2O_4$ samples, respectively. $NiFe_2O_4$ is a completely inverse spinel. Chappert and Frankel[3] have shown from their Mössbauer studies that is no canting of spins in $NiFe_2O_4$.

In this study, we present our Mössbauer and X-ray results on slowly cooled $Ni_xCo_{1-x}Fe_2O_4$ with special emphasis on atomic migration as a function of temperature and on the Debye temperatures for A and B sites.

II. EXPERIMENTAL

The slowly cooled $Ni_xCo_{1-x}Fe_2O_4$ samples were prepared by direct reaction of the elements in an evacuated quartz tube. The starting materials were high-purity Fe_2O_3(99.995%), NiO (99.999%) and CoO(99.999%). Mixtures of the elements in the proper proportions were sealed in evacuated quartz ampoules, heated at 1000 ℃ for 2 days, and then slowly cooled to room temperature at a rate of 10 ℃/h. In order to

obtain a homogeneous material, it was necessary to grind the samples after the first firing and to press the powders into pellets before annealing them for a second time in evacuated and sealed qurtz ampouls. The Mössbauer spectra were recorded using a conventional Mössbauer spectrometer of the electromechanical type[4] with a 10 mCi ^{57}Co source in a Rh matrix. The low temperature was obtained using an APD CS-202 displex closed-cycle refrigeration system with a DMX-20 Mössbauer vacuum shroud interface, and the temperature controller was a model DRC-91C manufactured by Lake Shore Cryotronics, Inc.

III. RESULTS AND DISCUSSION

X-ray diffraction patterns of the samples were obtained in the θ-2θ geometry with CuK α radiation. A slow scanning speed (0.25 ° advance in 2 θ per min.) was used to optimize resolution of closely spaced reflections. The lattice constant(a_0) for each composition as found by plotting $a_0(\theta)$ against the Nelson-Riley function[5] and extraploating to θ=90 ° . The results are shown in Fig.1. The lattice constant(a_0) decreases linearly with increasing nickel concentration(x) and follows Vegard's law approximately. This can be expected in view of the fact that the ionic radius of 0.69 Å for Ni^{2+} ions is smaller than that of 0.78 Å for Co^{2+} ions.
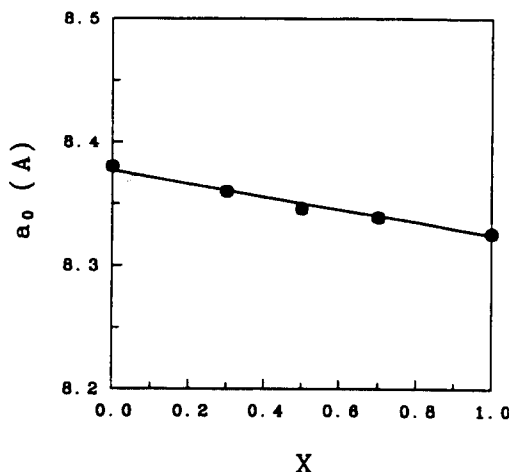
The most characteristic Mössbauer spectra of

Fig. 1   Lattice constans a_0 of $Ni_xCo_{1-x}Fe_2O_4$ at room temperature.

Table I . Isomer shifts δ, quadrupole shifts ΔE_Q, and magnetic hyperfine fields H_{hf} at various temperature T for $Ni_{0.3}Co_{0.7}Fe_2O_4$. δ is relative to the iron metal.

T(K)	δ (mm/s)		ΔE_Q(mm/s)		H_{hf}(kOe)	
	A	B	A	B	A	B
13	0.25	0.38	-0.01	-0.01	516	555
77	0.25	0.35	-0.01	-0.02	512	553
180	0.20	0.32	-0.02	-0.02	509	547
295	0.13	0.25	-0.01	-0.02	497	528
400	0.07	0.18	-0.01	-0.03	475	500
500	0.01	0.10	-0.01	-0.01	447	463
700	-0.10	-0.04	-0.01	-0.03	361	365

$Ni_{0.3}Co_{0.7}Fe_2O_4$ at various temperatures ranging from 13 to 800 K are shown in Figs. 2 and 3. The Mössbauer spectra are composed of two six-line hyperfine patterns A and B. Using a least-squares computer program, two sets of six Lorentzian lines were fitted to the Mössbauer spectra under the usual constraints[6], which are valid when the quadrupole interaction is much weaker than the magnetic hyperfine interaction. The results of the computer analysis are presented in Table I . The isomer-shift values at room temperature for A and B patterns in $Ni_{0.3}Co_{0.7}Fe_2O_4$ are found to be 0.15 and 0.26 mm/s relative to the Fe metal, respectively, which are consistent[7] with the high-spin Fe^{3+} charge state. The smaller value of
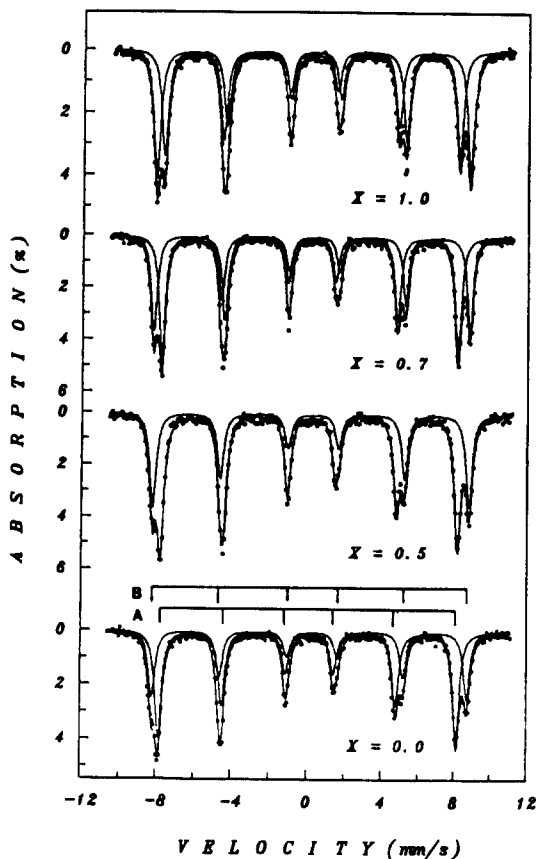

Fig. 2   Mössbauer spectra of $Ni_xCo_{1-x}Fe_2O_4$ at room temperature.

A-site isomer shift is due to a larger covalency at the A site.

Fig. 4 shows the temperature dependence of the magnetic hyperfine fields of the A and B sites for $Ni_{0.3}Co_{0.7}Fe_2O_4$. The field values at 13 K for the A and B sites are found to be 516 $\pm$ 2 and 555 $\pm$ 2 kOe, respectively, which are typical values for Fe^{3+} ions. It is noteworthy that in Fig. 2 and Table I , the quadrupole shift for both the A and B patterns vanish in accord with the cubic structure of $Ni_xCo_{1-x}Fe_2O_4$.

Fig. 5 shows the temperature dependence of the absorption area ratio of the A pattern to the B pattern.

The cation distribution of $Ni_{0.3}Co_{0.7}Fe_2O_4$ is $(Co_yFe_{1-y})^A(Co_{0.7-y}Ni_{0.3}Fe_{1+y})^BO_4$, indicating that y Fe ions have migrated from A to B sites. The area ratio of A and B subspectra for the above
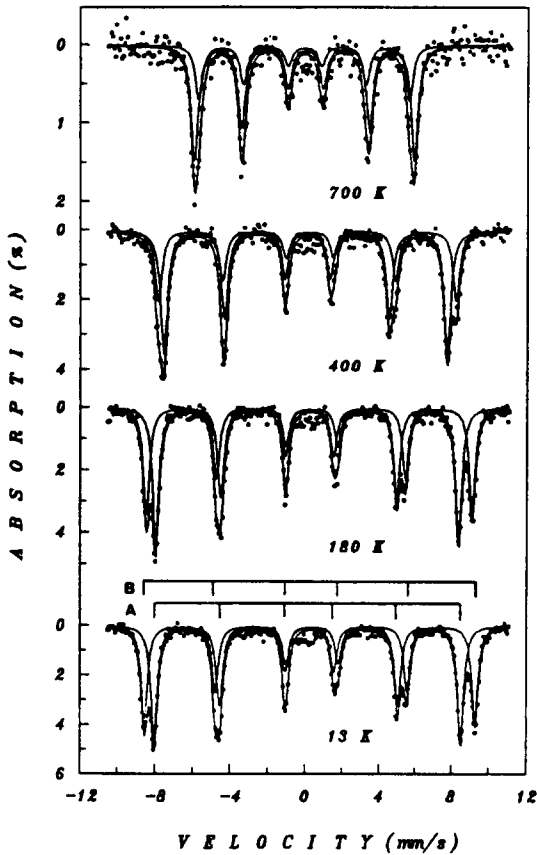
Fig. 3   Mössbauer spectra of $Ni_{0.3}Co_{0.7}Fe_2O_4$ at various temperature.
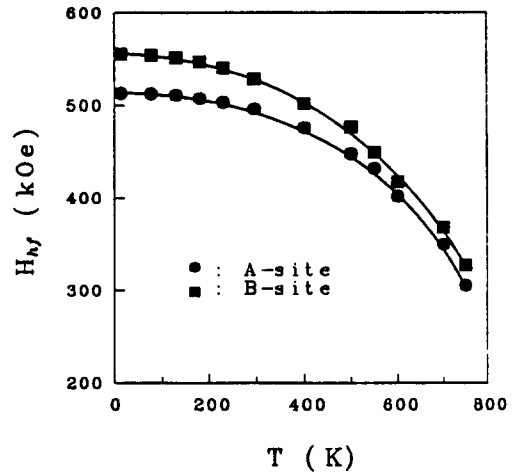

Fig. 4   Temperature dependence of the magnetic hyperfine field for $Ni_{0.3}Co_{0.7}Fe_2O_4$.
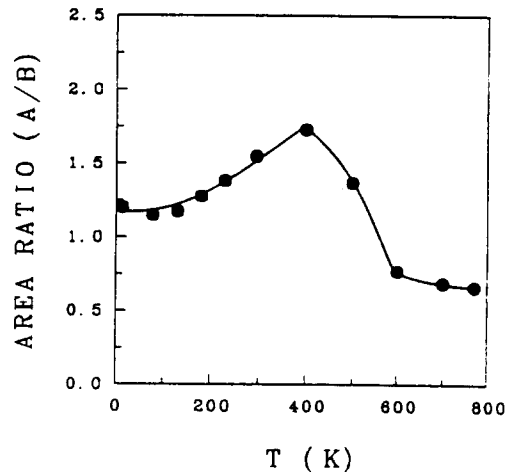
Fig. 5   Temperature dependence of the area ratio of A to B sites for $Ni_{0.3}Co_{0.7}Fe_2O_4$.

distribution is

$$\frac{I_A}{I_B} = \frac{(1-y)f_A}{(1+y)f_B} , \qquad (1)$$

where f_A and f_B represent the recoil-free fraction of A and B-site Fe ions, respectively. The Debye model gives the following expression for the recoil-free fraction[8] :

$$\ln f = -\frac{3E_R}{2k_B\theta}\left(1 + \frac{4T^2}{\theta^2}\int_0^{\theta/T}\frac{xdx}{e^x-1}\right) \qquad (2)$$

where E_R is the recoil energy of ^{57}Fe for the

Table II. Debye temperatures $\theta(K)$ for $Ni_xCo_{1-x}Fe_2O_4$.

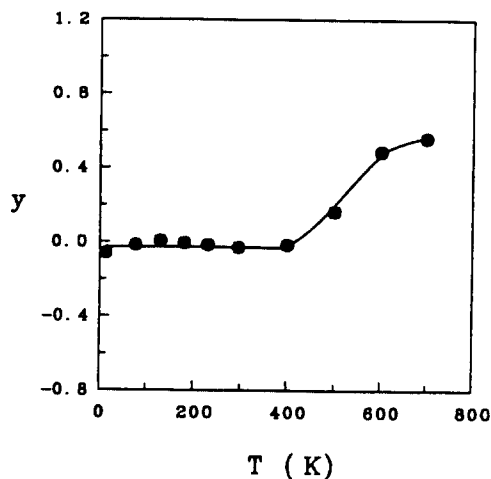| $\theta(K)$ \ x	0.0	0.3	0.5	1.0
θ_A	735	565	441	378
θ_B	248	285	321	357

Fig. 6　Temperature dependence of the fraction
y of the tetrahedral-site Fe^{3+} ions that
migrate to B sites for $Ni_{0.3}Co_{0.7}Fe_2O_4$.

14.4 keV gamma ray. θ and k_B represent the
Debye temperature and the Boltzmann constant,
respectively.

The Debye temperature for each site can be
calculated from the temperature dependence of
the resonant absorption area of each subsepctrum
at low temperatures.

The Debye temperatures are listed in Table II.
It can be seen in Table II that the Debye
temperature decreases with increasing nickel
concentration x. Ni ions replacing Co ions seem
to weaken the interatomic binding force between
Co and O ions.

Fig. 6 shows that atomic migration of
$Ni_{0.3}Co_{0.7}Fe_2O_4$ starts near 450 K in increases
rapidly with increasing temperature to such a
degree that 61 % of the iron ions at the A sites
move over to the B sites at 700 K. This onset
temperature is higher by about 50 K than the for
$CoFe_2O_4$. An implication of this result is that
increased Ni concentration enervates atomic
migration.

ACKNOWLEDGEMENTS

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