SOVIET PHYSICS JETP VOLUME 32, NUMBER 5 MAY, 1971

MÖSSBAUER INVESTIGATION OF COBALT FERRITE-CHROMITES

V. F. BELOV, N. S. OVANESYAN, V. A. TRUKHTANOV, M. N. SHIPKO, E. V. KORNEEV, V. V. KOROVUSHKIN, and L. N. KORABLIN

Institute for Crystallography, USSR Academy of Sciences; Institute for Chemical Physics, USSR Academy of Sciences

Submitted May 14, 1970

Zh. Eksp. Teor. Fiz. 59, 1484—1489 (November, 1970)

Cobalt ferrite-chromites are investigated by the Mössbauer effect technique. It is shown that exchange interactions between ions exert a strong effect on the hyperfine structure of the Mössbauer spectra. Good agreement between the experimental magnetic moments and those calculated on the basis of the Néel model can be attained in the presence of antiparallel ordering of spins in the B sublattice. At sufficiently high Cr^{3+} concentrations, exchange interaction fluctuations exert a large influence on the magnitude of the resulting saturation magnetization.

IN the literature there are a number of papers devoted to the investigation of ferrite-spinels by the Mössbauer effect.[1-3] The results of these investigations show that one can obtain two values of the magnetic field at the Fe^{57} nuclei situated on tetrahedral (A) and octahedral (B) sites and determine the temperature dependence of the hyperfine field in each of the sublattices. However, substituted ferrites are more interesting from the point of view of magnetic interactions. This is because the local field at the nucleus (and consequently the mean value of the ionic spin $\langle S_z \rangle$) is sensitive not only to the nearest-neighbor oxygens, but also depends on the number and kind of cations in the second coordination sphere.[4,5]

Replacement of the magnetic ions (Fe^{3+}) by nonmagnetic ones leads to a weakening of the indirect exchange interaction and, consequently, to a change in the hyperfine field, depending on the composition of the immediate surroundings. Introduction of Cr^{3+} ions, which have unfilled e_g orbitals, into a ferrite (just as in the case of nonmagnetic atoms) diminishes the exchange interaction. It is known that Cr^{3+} ions in the spinel structure under the influence of the ligand field are arranged exclusively in the octahedral sites as a consequence of a very high stabilization energy.

We have investigated a system of cobalt ferrite-chromites having the general chemical formula $CoFe_{2-x}Cr_xO_4$, where x varies from 0 to 2. An interesting peculiarity of this system is that the experimentally measured saturation magnetization does not agree with collinear ordering of the spins.

The samples were prepared by the usual methods of ceramics, using iron oxide Fe_2O_3 enriched to 30% Fe^{57}. The Mössbauer spectra were taken in an ordinary electrodynamic instrument with a Co^{57}(Pd) source. The spectra were analyzed by the least squares method, using a BÉSM-4 computer.

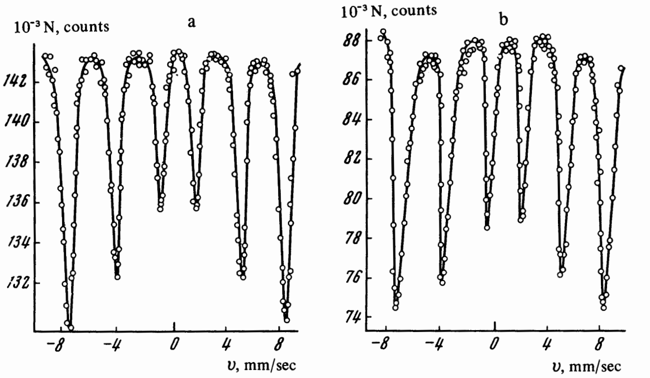

FIG. 1. Mössbauer spectra of $CoCr_xFe_{2-x}O_4$ taken at room temperature: a—x = 0, b—x = 0.6.

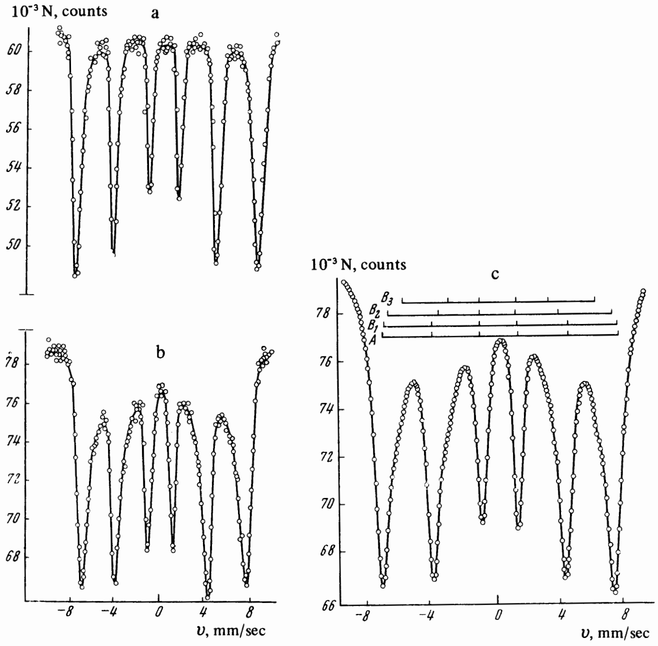

FIG. 2. Mössbauer spectra of Co $CrFeO_4$: a—T = 25°C; b—T = 196°C; c—T = −196°C, computer processed.

Figures 1—3 show the spectra of this ferrite system. The spectrum of Co-ferrite (x = 0) consists of six somewhat broadened components (Fig. 1a). This compound has a structure similar to the structure of an inverted spinel, i.e., there are approximately equal numbers of Fe^{3+} ions in the tetra- and octahedral positions. The hyperfine structure of the two different kinds of Fe^{3+} is

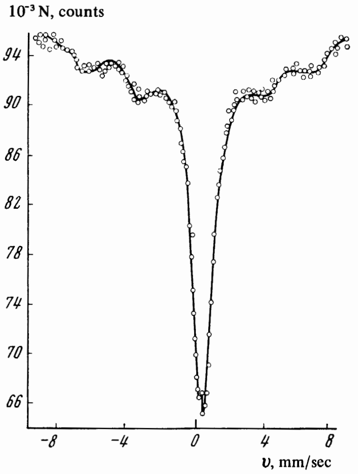

FIG. 3. Mössbauer spectrum of $CoCr_{1.5}Fe_{0.5}O_4$. Room temperature.

not resolved because the parameters of the hyperfine interaction for Fe^{3+} ions in A and B sites are close. For the sample with x = 0.6 (Fig. 1b), the inner sides of the components are not as steep as the outer sides.

As the chromium content is increased (x = 1) the asymmetry of the outer lines increases (Fig. 2a). At the top of Fig. 2c are plotted the positions of the centers of the hyperfine structure components, obtained by decomposition of the experimental spectrum by a computer programmed to decompose the spectrum into four sextuplets (A—the spectrum from Fe^{3+} in A sites; B_1, B_2, B_3—the spectra from octahedral Fe^{3+} sites). If one starts from the usually accepted cationic distribution $Fe^{3+}[CoFe_{1-x}Cr_x]O_4$ for $0 \leq x \leq 1$, he expects six narrow components from octahedral iron ions for x = 1. From Fig. 2a it is seen that the spectrum for this compound has broad and asymmetrical lines, however. It can be assumed that in this composition Fe^{3+} ions with different numbers of exchange couplings and consequently with different values of magnetic fields at Fe^{57} nuclei are present. The superposition of the spectra from these ions leads to broadening and asymmetry of the absorption lines.

For the identification of the components of the spectrum from iron ions located in different crystallographic positions, we measured the Mössbauer spectra in an external magnetic field H = 17 kOe perpendicular to the beam of γ rays. The magnetic moments of the Fe^{3+} ions in octahedral sites are then parallel to the magnetic field, whereas those in the tetrahedral sites are antiparallel. Hence, the outer spectral components from tetra- and octahedral nuclei are shifted in the external field in opposite directions: the tetrahedral lines move toward higher fields, and the octahedral ones toward lower fields. These measurements were made for a sample of $CoCrFeO_4$.

Taking into account that the width of the tetrahedral components in ferrite-spinels is less than the width of the octahedral lines, we can conclude that the outer tetrahedral line of A is located on the outer sides of the spectral components (Fig. 2a). This is confirmed by the displacement of the outer side of the spectrum toward higher fields and the increase in slope of the inner sides in an external magnetic field (Fig. 4). In this case the octahedral Fe^{3+} ions have a smaller magnetic local field $H_l(B)$ than the tetrahedral $H_l(A)$. The cation distribution calculated from the intensities of the A and B spectra has the form $(Co_{0.8}Fe_{0.2})[CrFe_{0.8}Co_{0.2}O_4]$. The parentheses indicate the tetrahedral and the brackets the octahedral ions. Replacement of Fe^{3+} ions by Cr^{3+} ions begins already at $x \leq 1$ to lead to the transfer of Co^{2+} ions from B to A positions, i.e., to a reduction of the degree of inversion.

The fact that $H_l(A) > H_l(B)$ indicates the stronger influence on the magnitude of the exchange energy (and consequently on the mean value of the spin $\langle S_z \rangle$ in the B sublattice) exerted by the tetrahedral Co^{2+} ions than by the octahedral Cr^{3+} ions. This is natural, since each A cation is coupled by twelve exchange bonds with the nearest B cations, whereas the B cations have only six exchange bonds with the closest tetrahedral ions. The transfer of Co^{2+} ions to A positions is accompanied by a great reduction in the exchange bonds and consequently to a decrease in the magnetic field at the octahedral nuclei compared to the magnetic field acting on the tetrahedral nuclei.

The analysis of the broad spectral components from the octahedral iron ions in $CoFeCrO_4$ showed that it is necessary to take into account also the inequivalence of the direct B—B bonds. The probability that an octahedral ion has 0, 1, or 2 Fe^{3+} ions as its nearest neighbors among the six nearest tetrahedral ions is $P_0 = 0.29$, $P_1 = 0.43$, or $P_2 = 0.27$, respectively. These probabilities are proportional to the intensities of the corresponding sextuplets. In this case, it is obvious that the hyperfine structure with relative intensity determined by probability $P_2 = 0.27$ corresponds to the greater magnetic field.[5] The Fe^{3+}(B) ions also differ with respect to the composition of cations in the first sphere, the interaction between which occurs by overlap of the t_{2g} orbitals. The direct interactions $Cr^{3+}-Cr^{3+}$, $Fe^{3+}-Cr^{3+}$, and $Fe^{3+}-Fe^{3+}$ of ions in B sites, according to[6], can be antiferromagnetic, whereas $Co^{2+}-Fe^{3+}$ and

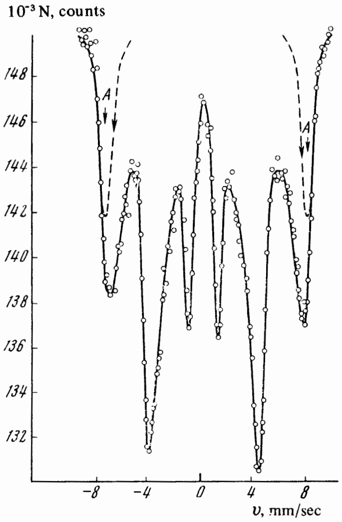

FIG. 4. Mössbauer spectrum of $CoCrFeO_4$ taken in an external magnetic field H = 17 kOe.

$Co^{2+}-Cr^{3+}$ are ferromagnetic.[1)] Since the content of Co^{2+} in the B sublattice for compositions $x \geq 1$ is relatively small, we can neglect the ferromagnetic interactions $Co^{2+}-Fe^{3+}$ and $Co^{2+}-Cr^{3+}$ and consider only the negative interaction of the type $Cr^{3+}-Cr^{3+}$, $Fe^{3+}-Cr^{3+}$.

As already noted, for Co-ferrite-chromite with $x \leq 1$ a collinear Néel ordering of the spins is accepted. However, the saturation magnetization per formula unit calculated according to the Néel model for the distribution $(Co_{0.8}Fe_{0.2})[CrFe_{0.8}Co_{0.2}]O_4$ gives the value $n_V = 4.5\ \mu_B$, whereas the experimental value is $1\ \mu_B$.[7] Such a large discrepancy cannot be explained solely by a non-collinear spin arrangement. We obviously have to take into account spins with antiparallel ordering (antiferromagnetic interaction) in the B sublattice. Good agreement between the calculated and experimental values of n_V can be obtained if it is assumed that the direction of the magnetic moments of the Fe^{3+} and Cr^{3+} ions located in B sites becomes antiparallel to the resultant spin of the B sublattice when these ions have five and six possible immediate neighborhoods with tetrahedral Cr^{3+} ions.

Decrease of temperature to 85 K leads to a narrowing of the spectral components (Fig. 2b), since at small values of T/T_c with an increase in the average exchange energy (and consequently $\langle S_z \rangle$), the hyperfine field is almost independent of the inhomogeneity of the immediate cationic neighborhood.

Another important feature of the Mössbauer spectra of the $CoCr_xFe_{2-x}O_4$ system we investigated is the presence of a doublet in the sample with x = 1.5 at T = 300 K (Fig. 3). The existence of a doublet along with a six-line spectrum is due to electronic spin relaxation processes. The electronic relaxation time is comparable in magnitude or smaller than the Larmor precession period of the nuclear spin of Fe^{57}. As a consequence of the high concentration of Cr^{3+} ions in $CoFe_{0.5}Cr_{1.5}O_4$, a significant portion of the exchange bonds of tetrahedral Fe^{3+} ions is weakened on account of the interaction with Cr^{3+} ions. Comparison of the spectra of Co-ferrites having different chromium concentrations showed that those $Fe^{3+}(A)$ ions for which ten or more of the nearest B sites are occupied by Cr^{3+} ions contribute to the doublet part of the spectrum. The difference in the neighborhoods of the Fe^{3+} ions leads to fluctuations of the exchange interaction. In this case, the ferrite has not one, but a whole series of Curie temperatures, and the sample is a magnetically heterogeneous system.

The analysis of the six-line spectrum of $CoFe_{0.5}Cr_{1.5}O_4$ showed that it cannot be described by a spin Hamiltonian that takes into account quadrupole interaction and magnetic dipole interaction of the collinear magnetic moments of the ions. For the other compositions it was possible to measure the Mössbauer spectral parameters only for the tetrahedral iron nuclei. These results are:

x:	0	0,6	1,0	1,5
ΔE_Q:	0	0	0	—
H_l, kOe:	496±5	480±5	446±8	400±8

It is seen that the quadrupole shifts ΔE_Q for $Fe^{3+}(A)$ are approximately zero and do not change when x changes from 0 to 1. This is a natural situation, since the magnitude of the quadrupole shift in the case of axial symmetry of the electric field gradient (EFG) is proportional to $(3\cos^2\theta - 1)$, where θ is the angle between the direction of the magnetic field $H_l(A)$ and the EFG axis. The quadrupole splitting becomes zero when the angle θ is 55°. Thus, in these compositions, the magnetic field H_l is directed along [111], and the symmetry axis of the EFG coincides with [100], i.e., in the compounds investigated there is a collinear ordering of the spins in the A sublattice. In the paramagnetic region (sample with x = 0.5) a doublet appears with quadrupole splitting approximately equal to 0.2 mm/sec, evidence that local symmetry deviates from cubic. These deviations are not so great as in the nickel ferrite-chromites, in which the quadrupole splitting is 0.5 mm/sec.

Thus, the investigation we have made of the $CoFe_{2-x}Cr_xO_4$ system shows that when iron ions are replaced by Cr^{3+} ions, there is a transfer of Co^{2+} ions from octa- to tetrahedral positions. As a result, $H_l(A)$ is greater than $H_l(B)$.

Satisfactory agreement between the experimental and theoretical values of μ_B for the compositions with $x \leq 1$ is achieved in the presence of partial antiparallel ordering in the B sublattice. In the tetrahedral sublattice, the spins have collinear Néel ordering.

For the compositions with $x > 1$, the existence of a doublet together with the six-line spectrum is due to processes of electronic relaxation of Fe^{3+} ions with weakened exchange couplings.

In the cobalt ferrite-chromites, a deviation of the symmetry of the local neighborhood of iron ions from cubic is observed.

In conclusion, the authors thank V. I. Gol'danskiĭ, Associate Member of the USSR Academy of Sciences, for a helpful discussion of the results.

[1] B. Evans, S. Hüfner, and G. Kalvius, Phys. Lett. **23**, 24 (1966).

[2] G. Sawatsky, F. van der Woude, and A. Morrish, Phys. Lett. **A25**, 147 (1967).

[3] J. Morel, J. Phys. Chem. Solids **28**, 629 (1967).

[4] L. Cser, J. Dezsi, J. Gladkin, L. Keszthelyi, D. Kulgawczyk, N. A. Eissa, and E. Sterk, Phys. Stat. Sol. **27**, 131 (1968).

[5] G. A. Sawatsky, F. van der Woude, and A. H. Morrish, J. Appl. Phys. **39**, 1204 (1968).

[6] G. V. Novikov, B. A. Trukhtanov, L. Cher, S. I. Yushchuk, and V. I. Gol'danskiĭ, Zh. Eksp. Teor. Fiz. **56**, 743 (1969) [Sov. Phys.-JETP **29**, 403 (1969)].

[7] J. B. Goodenough, Phys. Rev. **117**, 1442 (1960).

Translated by L. M. Matarrese
170

[1)] It is shown in [6] experimentally that ferromagnetic B–B interactions between Ni^{2+} and Fe^{3+} exist.