Multiplet splitting of mixed spinels $NiFe_xCr_{2-x}O_4$ and its relation to magnetic hyperfine fields*

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The x-ray photoelectron spectra of Ni $3s$ and Cr $3s$ for the mixed spinels $NiFe_xCr_{2-x}O_4$ ($0 \leq x \leq 2$) were measured at room temperature. The multiplet splitting of Ni $3s$ was compared with an average magnetic hyperfine field determined by Mössbauer spectroscopy. It is found that the multiplet splitting is nearly constant as a function of chemical composition. This suggests that the large values found for the hyperfine field on tetrahedral sites may be due to orbital contributions.

I. INTRODUCTION

In systems with unpaired valence electrons the exchange interaction between these and core electrons unequally affects spin-up and spin-down core electrons. This causes a multiplet splitting of their binding energies. By means of XPS (x-ray photoelectron spectroscopy) this splitting can be measured. This experimental method has been successfully applied for the study of multiplet splitting of transition-metal complexes and the effects of their chemical environment.[1-3]

This exchange interaction also gives rise to a spin polarization which produces different radial functions for different spins and results in a net spin density in each of the core shells. This spin density is finite at the nucleus for the core s electrons and produces, via the Fermi contact interaction between the nuclear and electronic spin, a contribution to the magnetic hyperfine field at the nucleus. In addition to this contact term, the magnetic hyperfine field has contributions from orbital and dipolar terms.

The magnetic hyperfine field of the Ni cations for the spinel samples $NiFe_xCr_{2-x}O_4$ ($0 \leq x \leq 2$) has been measured by the Mössbauer technique[4] and the multiplet splitting for the $3s$ shell of Ni has been measured using XPS by ourselves. The multiplet splitting is proportional to the contact term, as has been verified experimentally in certain instances.[5] Thus, by using XPS, one is able to follow the variations in the contact term and in this way increase our understanding of the sources for the magnetic hyperfine field.

II. EXPERIMENTAL PROCEDURE

The core-shell photoelectron spectra of spinel samples $NiFe_xCr_{2-x}O_4$ were measured for $x = 0$, 0.5, 1, 1.5, 2. Al $K\alpha$ (1487 eV) and Mg $K\alpha$ (1254 eV) x-rays were used for ejecting the electrons. The main attention was put on the measurement of the energy differences between the pair of lines found with $3s$ spectra of Ni, Fe, and Cr ions. It was also necessary to take measurements on the $2p$ and $3p$ spectra in order to correct the presence of shake-up satellites, as will be explained in Sec. III.

The experiments were done on an electrostatic electron spectrometer located in the Physics Division at ORNL, which has been previously described.[6] The photoelectron spectra were fitted with Gaussian peaks using a Dupont 310 curve resolver. The samples were kindly supplied by F. E. Obenshain and are the same as those used in the measurement of the magnetic hyperfine field by means of Mössbauer spectroscopy.[4]

III. RESULTS AND DISCUSSION

Theoretical considerations

The normal spinel structure consists of tetrahedral (A) and octahedral (B) sites in a face-centered-cubic oxide sublattice AB_2O_4, where A is a divalent metal ion and B is trivalent. Eight A sites and sixteen B sites are occupied in one unit cell. In an inverse spinel structure, on the other hand, trivalent ions occupy the A sites, and the B sites contain eight trivalent and eight divalent ions.[7] The cation distribution in the spinel samples under study is given by the formula

$$(Ni_{1-x}^{2+}Fe_x^{3+})[Ni_x^{2+}Cr_{2-x}^{3+}]O_4 \quad \text{for } 0 \leq x \leq 1. \quad (1)$$

Ions in ( ) are on A sites and those in [ ] are on B sites. For $x > 1$, Ni^{2+} and Cr^{3+} are both on B sites.[8]

The magnetic hyperfine field is formed by several contributions of which the most important are the contact term (H_c), the orbital term (H_L), and the dipolar term (H_D), of which the last is negligible.[9] Owing to the exchange interaction, the core electrons with the same spin experience a larger effect than do the electrons with opposite spin. This creates different radial wave functions for different spins and a net spin density $|\psi_i(r)|^2 - |\psi_i(r)|^2$ in each of the core shells will result. The spin density is finite at the nucleus for the core s electrons and produces, via the Fermi contact interaction a magnetic hyperfine field, the so-called Fermi contact term. The expression of this

TABLE I. Theoretical contributions to the contact term for Ni^{2+} (see Ref. 11).

Shell	H_c (kG)		Percentage[a] of change in H_c
	Free Ni^{2+}	Ni^{2+} in a cubic field	
$1s$	-22.7	-26.9	-1.3%
$2s$	-810.0	-850.4	-12.2%
$3s$	$+500.9$	$+602.0$	$+30.5\%$
Total	-331.8	-275.3	$+17\%$

[a]Relative to total $=-331.8$ kG.

hyperfine magnetic field is given by[10]

$$H_c = -\tfrac{16}{3}\pi\mu_B \sum_{ns \text{ shells}} \langle |\psi_{ns}\!\uparrow(0)|^2 - |\psi_{ns}\!\downarrow(0)|^2 \rangle , \qquad (2)$$

where the expression contained in brackets is the expectation value for the spin density and μ_B is the Bohr magneton. From this expression one can see that H_c is made-up by the contribution of the s shells. An equivalent expression is[10]

$$H_c = 2S\chi , \qquad (3)$$

where S is the total spin and χ is the core-polarization field per unpaired spin; χ is approximately constant for each of the transition-metal series. The expression for the orbital contribution is given by

$$H_L = -\mu_B\langle 1/r^3\rangle\langle g - 2.0023\rangle\langle S\rangle , \qquad (4)$$

where g is the gyromagnetic ratio and $\langle S\rangle$ is the expectation value of the spin.

It is theoretically difficult to do calculations for these two terms in the case of the spinel samples. However, theoretical calculations of H_c have been done using spin-polarized Hartree-Fock functions for free Ni^{2+} and Ni^{2+} in a cubic field.[11] The calculation of the contributions from the individual shells to the contact term are shown on Table I. The change in percentage in going from the free ion Ni^{2+} to Ni^{2+} in a cubic field is also shown in the fourth column of the table. The contribution from the $1s$ shell is negligible. The contribution from the $2s$ shell is large and of opposite sign to that from the $3s$ shell. However, the main change in the hyperfine field is related to the behavior of the $3s$ shell.

When a $3s$ hole is formed in a first-row transition-metal compound, the exchange interaction will produce a different effect on spin-up and spin-down electrons, and two final states will result. Largest energy separation occurs when both unfilled shells have the same principal quantum number. From atomic multiplet theory[12] the exchange interaction between i and j electrons is given by

$$K_{ij} = \delta(ms_i, ms_j)\sum_{k=0}^{\infty} [C^k(l_i ml_i; l_j ml_j)]^2$$
$$\times G^k(n_i l_i; n_j l_j) , \qquad (5)$$

where $C^k(l_i m_{l_i}; l_j m_{l_j})$ is a Clebsch-Gordon coefficient and $G^k(n_i l_i; n_j l_j)$ is the Slater exchange integral. This expression shows that only the parallel spins will be affected; therefore, the splitting due to the exchange interaction between $3s$ and $3d$ electrons is $\Delta\epsilon = \tfrac{1}{5}(2S+1)G^2(3s, 3d)$, where S is the total spin for the ground state and the Slater exchange integral is given by

$$G^2(3s, 3d) = \int_0^\infty \int_0^\infty R_{3s}(r_1)R_{3d}(r_2)R_{3s}(r_2)R_{3d}(r_1)$$
$$\times (2r_<^2/r_>^3)r_1^2 r_2^2 \, dr_1 \, dr_2 , \qquad (6)$$

where R_{3s} and R_{3d} are the radial wave functions for the respective orbitals. Spin-unrestricted Hartree-Fock (SUHF) calculations of the difference in total energy between the two final states have been done for free ions. The theoretical results are about twice as large as the experimental measurements. However, when the effect of configuration interaction is included, the calculations gave reasonably good agreement with the experimental results.[13]

From the theoretical discussion one expects the multiplet splitting and the Fermi contact interaction to be closely related in such a way that measuring the multiplet splitting one can follow the variations of the contact term. For example, it has been found that the multiplet splitting is proportional to the Fermi contact term for the simple case of spin-only compounds.[5]

Experimental results

As examples of the data taken with XPS spectra of Ni $3s$ for the spinels $NiCr_2O_4$ and $NiFe_2O_4$ are shown on Fig. 1. In addition to multiplet splitting, satellite structure may also contain contributions from electron shake up. Therefore the $2p$ and $3p$ spectra were measured in order to correct for shake-up contribution in the $3s$ spectra. The following assumptions are made: (i) The shake-up excitation energy is independent of the inner-shell vacancy and can be derived from the $2p$ spectrum of the metal ion. (ii) The intensity for electron shake up is about the same for photoionization in the $3s$ or $3p$ shells, but about 3 times larger for K and L shell holes. This has been verified experimentally.[14,15] Theoretically, the total shake-up plus shake-off probabilities have been calculated for nickel ions (cf. Table II) making use of the sudden approximation and relativistic Hartree-Fock-Slater wave functions. These calculations also support our assumption. Using the excitation energy for shake up as found in the $2p$ spectra, the $3p$ spectrum was deconvoluted and the amount of shake-up
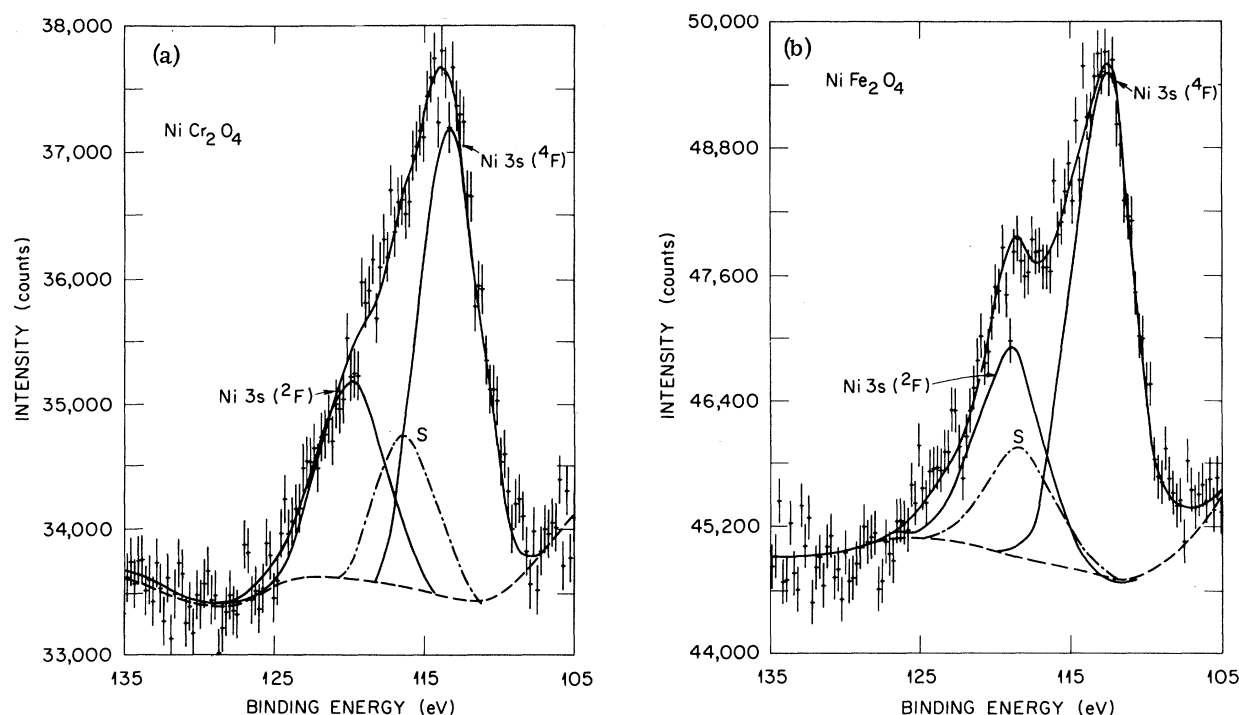
FIG. 1. Ni 3s photoelectron spectra of the spinels $NiCr_2O_4$ (a) and $NiFe_2O_4$ (b). The multiplet splitting peaks are indicated with solid lines, the shake-up peaks S with dash-dot lines, and the background including contribution from the Fe 3s peaks or Si contamination with dash lines. Since the peaks ride on a large flat background of secondary electrons, the ordinate exes are plotted from a finite background rather than zero for easier viewing.

estimated. It was then supposed that the same contribution is present in the 3s spectrum.

After corrections for contributions from electron shake up, the spectra shown in Fig. 1 are deconvoluted on the assumption that only two peaks will be present, due to multiplet splitting in atoms having a single chemical environment. This assumption is made since there should be Ni ions only on site B for $NiCr_2O_3$, and for $NiFe_2O_4$ there should be nickel ions only on site A. The uncertainty for determining multiplet splitting by deconvolution in the two spectra is about 1–1.5 eV, or an error of about 20–30%, which is to be contrasted with changes of 400–500% in the hyperfine fields as measured by a Mössbauer experiment.[4] For some of the other spinels there could be, in principle, two pairs of peaks due to two different sites, but no evidence of such pairs was seen.

The multiplet splitting values for Ni, Fe, and Cr are given in Table III together with the ratios of the two multiplet peaks. In the case of Ni^{2+} $(3d^8)$ there are two unpaired spins, either in octahedral or tetrahedral coordination[16]; and the two possible final states after the ejection of a 3s electron are ^4F and ^2F. With five unpaired spins in the ground state Fe^{3+} $(3d^5)$, has two possible final states, ^7S and ^5S, when a hole is made in the 3s shell. For

Cr^{3+} $(3d^3)$ with three unpaired spins, the final states with a hole in the 3s shell are ^5F and ^3F. Ideally, the ratio of intensities will be equivalent to the multiplicities, but actually this value may be slightly higher due to electron correlation effects.[13]

The principal deduction from Table III is that the energy splitting of the nickel lines is essentially constant. The multiplet splittings for Cr and Fe were also measured in order to compare with

TABLE II. Probability for electron shake up plus shake off (%)[a] for 3d shell as a function of inner-shell vacancy of Ni^{2+}.

Inner-shell vacancy	Probability[a] (%)
1s	9.9
2s	10.4
$2p_{1/2}$	10.6
$2p_{3/2}$	10.6
3s	4.7
$3p_{1/2}$	4.6
$3p_{3/2}$	4.5

[a]For further information on the nature of these calculations, see T. A. Carlson and C. W. Nestor, Jr., Phys. Rev. A <u>8</u>, 2887 (1973).

TABLE III. Experimental energy separations and intensities for the $3s$ shells of Ni, Fe, and Cr from the spinel samples $NiFe_xCr_{2-x}O_4$.

Spinel	Ni $3s$ $\Delta\epsilon$ (eV)[a]	I[b]	Fe $3s$ $\Delta\epsilon$(eV)	I	Cr $3s$ $\Delta\epsilon$ (eV)	I
$NiCr_2O_4$	5.6	1.9			4.4	1.8
$NiFe_{0.5}Cr_{1.5}O_4$	5.4	1.7	...[c]	...[c]	4.4	1.8
$NiFeCrO_4$	5.6	1.9	7.6	2.4	4.6	2.3
$NiFe_{1.5}Cr_{0.5}O_4$	5.9	1.9	6.4	2.3	3.9	2.3
$NiFe_2O_4$	5.4	1.9	6.6	2.1		

[a]$\Delta\epsilon$ is the multiplet splitting.
[b]I is the ratio of intensities of the peaks representing the higher to lower spin states.
[c]Not available due to Si contamination.

the Ni results. In the case of Cr one might expect little change in splitting as a function of chemical composition, because the ion is always on octahedral site, and this is what is found, as shown in Table III. For iron there is a little change when Fe, Cr, and Ni are in the same proportion, but unfortunately due to Si contamination it was not possible to determine the multiplet splitting for iron in low concentration.

Multiplet splitting for nickel as a function of the chemical composition is shown in Fig. 2. From the large difference between the measured hyperfine magnetic fields for the two sites A and B of the spinel samples, one might expect to find two multiplet splittings, one for each site. Our experimental results show only one multiplet splitting; therefore the value for the multiplet splitting is the average contribution from the A and B sites. The average value of the magnetic hyperfine field is also plotted on this figure. This average value was taken from the values of the magnetic hyperfine field given in Ref. 4 and weighted by the relative concentration of A and B sites.

The contact term is expected to vary with the environment of the ion if due to Fermi contact interaction. However, the experimental data on Fig. 2 show that multiplet splitting is nearly constant for all the spinel samples; and, therefore, there is only a small change when the nickel coordination changes from tetrahedral to octahedral. However, there is a large change in the hyperfine magnetic field, which has a variation in the region $0 \leqslant x < 1$ and then keeps constant when nickel is on octahedral coordination.

As is shown on Table I, the main variation of the contact term with the environment is due to the $3s$ contribution; therefore, one expects the results for this shell to be representative of the total effect. Exchange splitting can be altered by correlation effects but though correlation reduces the splitting in the $3s$ shell it has been the general ex-

perience that this splitting follows the spin density rather well through a series of compounds.[2] Although there will remain some uncertainties, one expects that changes in multiplet splitting will follow the changes in the Fermi contact term. Our results show a fairly constant splitting as compared with a large change of the hyperfine field, measured by Mössbauer spectroscopy. Thus, we conclude that it is possible that the large changes in the hyperfine field found with the Mössbauer experiment may be due to orbital contributions. As to exactly why the orbital term would be highly sensitive to chemical environment is not entirely clear, but it is of interest to note that x-ray studies[17] of these spinels show that below 310 °K there is a competition between spin-orbit interac-
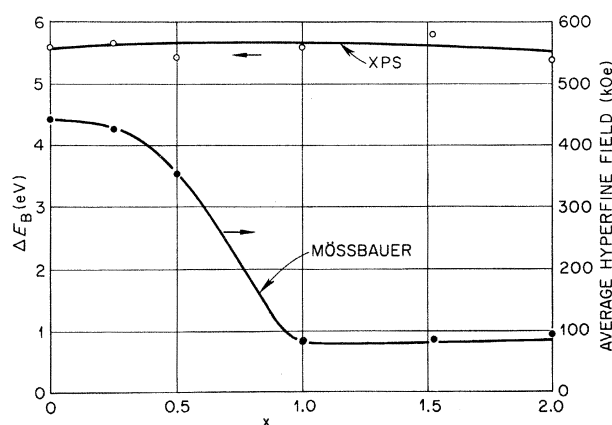

FIG. 2. Comparison of multiplet splitting and weighted average hyperfine magnetic field in nickel for the spinels $NiFe_xCr_{2-x}O_4$ as a function of Fe to Cr concentration. The left vertical scale corresponds to binding energy and the right to hyperfine magnetic field. Mössbauer data taken from Love and Obenshain, Ref. 4. Point at 1.0 is recent unpublished data from F. E. Obenshain and J. C. Love.

tion and the Jahn-Teller effect that causes a distortion in the lattice, which in turn changes the Ni gyromagnetic ratio g. This is highly speculative and given only as a suggestion as to the type of effect that might explain the sensitivity to the orbital term.

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