Observation of Spin-Polarized Electron Levels in Ferrites

S. F. Alvarado, W. Eib, F. Meier, D. T. Pierce, K. Sattler, and H. C. Siegmann
Laboratorium für Festkörperphysik, Eidenössiche Technische Hochschule Zürich, CH-8049 Zürich, Switzerland

and

J. P. Remeika
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 26 November 1974)

Measurement of spin polarization of photoelectrons from Fe_3O_4 (MAG) and $Li_{0.5}Fe_{2.5}O_4$ (LIF) up to $\hbar\omega = 11$ eV shows that B-site $3d$ levels are higher in energy than A-site $3d$ levels. In MAG, unpolarized $2p$ electrons are not emitted up to 11 eV. Existing energy diagrams of MAG do not agree fully with the results. As a direct consequence of Hund's rule, the polarization spectra of MAG and LIF are very different because of the presence of Fe^{2+} in MAG.

The electronic structure of ferrites is still a subject of speculation.[1] This arises because the classical methods for obtaining information on electronic structure are ambiguous, mainly because they cannot distinguish whether an optical transition is due to excitation of an oxygen p electron or of a metal-ion d electron, nor in which of the two existing sublattices (called A and B lattices) it occurs. Band theory is of little help because it is well known that it runs into difficulties with d levels. We report here on a new experiment employing measurement of photoelectron spin polarization (photo-ESP) that allows one (i) to decide whether an electron was excited from a metal ion in the A or B lattice, and (ii) to distinguish between excitation of p and d electrons. It is, to our knowledge, also the first photoemission experiment on single-crystal ferrites cleaved in ultrahigh vacuum, and the first photo-ESP study up to a photon energy $\hbar\omega = 11$ eV.

Measurements are reported for magnetite (MAG), $Fe^{3+}[Fe^{2+}Fe^{3+}]O_4$, and for lithium ferrite (LIF), $Fe^{3+}[(Li^+)_{0.5}(Fe^{3+})_{1.5}]O_4$. The comparatively large O ions form a fcc lattice. There are tetrahedral and octahedral interstitials called A and B sites, in which the metal ions are located. A sites have four oxygen ions as nearest neighbors and B sites have six. The metal ions in the square brackets are at B sites, and the remaining Fe^{3+} is at an A site. MAG and LIF are both inverse spinels. Néel showed that the magnetic coupling between A- and B-lattice ions is antiferromagnetic and much stronger than A-A and B-B coupling. Hence the magnetization is $M = M_B - M_A$. $Fe^{3+}(3d^5)$ has a spin-only moment of $5\mu_B$, and $Fe^{2+}(3d^6)$ has $4\mu_B$. For MAG, we have at $T = 0$ $M = 9 - 5 = 4$ (number n_B of Bohr magnetons per formula unit) and for LIF $M = 1.5 \times 5 - 5 = 2.5$. This agrees quite well with the observed magnetizations of 4.1 and 2.6, respectively,[2] which shows that the main part of M is generated by the spin of the d electrons. Fe^{3+} on the A site emits electrons with magnetic moment antiparallel to $\vec{M}$ only. We define this as negative ESP. This is how A-site emission is distinguished from B-site emission, which yields positive photo-ESP. In MAG, we have at B sites Fe^{2+} besides Fe^{3+}. Fe^{2+} has an extra electron whose magnetic moment is antiparallel to the magnetization according to Hund's rule. Emission of this extra electron produces negative ESP as well, although it stems from the B lattice. To identify the contribution of the extra electron on the B site we compare photo-ESP of MAG with that of LIF. In LIF, there is no Fe^{2+}, and photoemission from B sites produces positive ESP only. Otherwise, MAG and LIF are very similar. The lattice constants are $a = 8.39$ and 8.33 Å, respectively, and the oxygen parameters u describing the distortion of the fcc oxygen lattice by the different sizes of the ions are $u = 0.379$ and 0.382. (In the ideal fcc lattice $u = 0.375$; see Ref. 2.)

The contribution from oxygen p levels to the emission is detected by the fact that there is an equal amount of up and down spins in these orbitals, and the photo-ESP is zero. This may seem a very naive picture because of p-d hybridization. More precisely, we should say that we can distinguish magnetic and nonmagnetic electrons. However, since the counting of up- and down-spin d electrons yields reasonably well the observed magnetization, the naive picture should not be too bad.

The MAG crystals were natural single crystals from Zermatt, Switzerland. Buchenau and Müller[3] did optical studies on such crystals. The metal-insulator transition occurs at $T_v = 119°K$ which shows that the samples are reasonably pure. LIF crystals were grown in the ordered state. The samples were mounted in crystal holders, inserted into the ultrahigh-vacuum apparatus (~10^{-10} Torr), and transported to the cleavage chamber. After cleaving[4] with knife and anvil, the samples are transported into the magnetic field $\vec{H}$, which is perpendicular to the photoemitting surface. The light from a modified Hinteregger hydrogen-discharge lamp[5] or a Hg-Xe high-pressure arc is monochromatized through a McPherson 1-m spectrograph and focused onto the sample surface. The photoelectrons are accelerated and the ESP is measured by Mott scattering from Au nuclei at an energy of 100 keV as previously described.[6]

The ESP is defined as $P = (n_\uparrow - n_\downarrow)/(n_\uparrow + n_\downarrow)$, where $n_\uparrow$ and $n_\downarrow$ are the numbers of up- and down-spin-moment electrons. We can make two simple predictions about the dependence of P on photon energy $\hbar\omega$: (1) If all the magnetic electrons are emitted with equal probability and no unpolarized nonmagnetic electrons are admixed, we expect $P = n_B/n$, with n the total number of d electrons. This yields an ESP of 25% for MAG and 20% for LIF. (2) The electrical conductivity in MAG is assumed to be caused by some kind of hopping of the minority-spin electron introduced by Fe^{2+} in the B lattice.[1] Threshold photoelectrons originate from energy states near the Fermi energy E_F, and this is why one predicts negative ESP at threshold in MAG, but not in LIF.

These predictions make sense only if photoemission tests the bulk properties with MAG and LIF. The photoelectric probing depth is probably large in both materials, but still only a few atomic layers. It is a special feature of photo-ESP studies that information on contributions of the surface can be obtained by comparing well-known bulk magnetization curves with photoelectric magnetization curves. In $4f$-ferromagnetic insulators like EuO, photoelectric magnetization curves do not saturate, which means that the surface sheet has magnetic properties different from those of the bulk.[7] In MAG, photo-ESP was constant for $8 \leq H \leq 20$ kG within the accuracy of the measurement. Therefore, we think that there are no paramagnetic surface spins in ferrites that contribute appreciably to the photo-ESP, neither by direct photoemission nor by spin-exchange collisions. The difference between $3d$ and $4f$ materials can be understood by the difference in local extensions of the magnetic shells, and the very different exchange mechanisms.

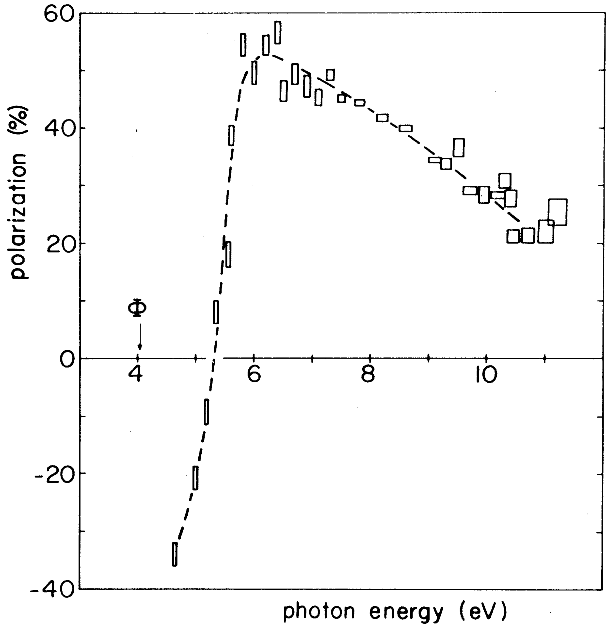

FIG. 1. Dependence of photoelectron spin polarization in percent on photon energy in eV for Fe_3O_4 at constant magnetic field strength $H = 8.5$ kG. The sample is at $T \cong 10°K$. Vertical extension of measured points indicates statistical uncertainty; horizontal extension, resolution of monochromator. Photothreshold Φ is indicated by arrow.

Figure 1 shows the spectrum of spin polarization (SSP) for MAG. There is negative ESP at threshold as predicted. For $\hbar\omega = 11$ eV, $P \cong 24\%$. This shows that emission of nonmagnetic or p electrons is negligible up to 11 eV. P reaches a maximum at $\hbar\omega \cong 6.5$ eV which indicates the energy of predominant emission from Fe^{3+} at B sites. Fe^{3+} A-site emission sets in at higher $\hbar\omega$, causing the decrease of P for $\hbar\omega > 6.5$ eV. The SSP of Fig. 1 was taken with the sample at ~10°K. The SSP at 300°K is quite similar except that the amplitude of P is lower in different parts of the spectrum, which is partly because of the decrease of sublattice magnetizations M_A and M_B with temperature. Further experiments on the temperature dependence of photo-ESP are being prepared. What can be said at present is that the statements on the energy of spin-polarized electron levels do not depend on whether MAG is in the metallic or the insulating state.

Figure 2 shows the SSP of LIF. The photothreshold Φ is almost identical to the one of

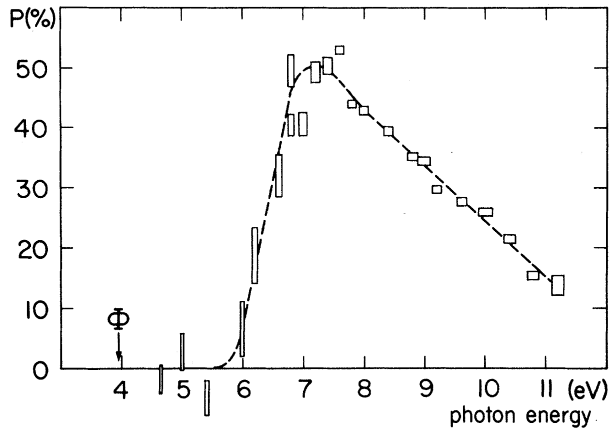

FIG. 2. Photo-ESP in percent versus photon energy in eV for $Li_{0.5}Fe_{2.5}O_4$ at $H = 8.5$ kG. The sample is at $T \cong 50$°K. Extension of measured points, see caption of Fig. 1.

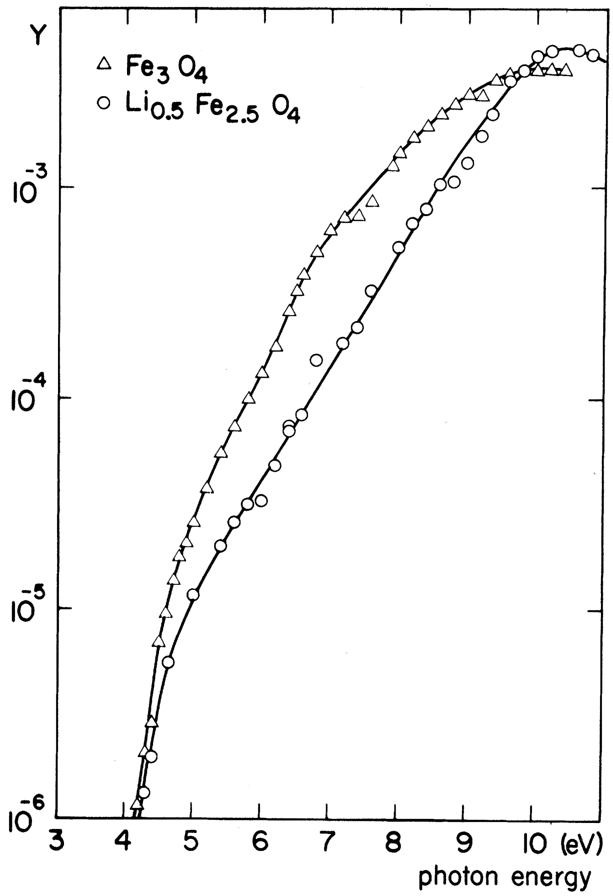

FIG. 3. Dependence of photoelectric yield Y (number of photoemitted electrons per incident photon) on photon energy in eV for MAG and LIF. Y is not corrected for mirror reflectance and window transmission.

MAG, but $P = 0$ for threshold electrons. Whether these nonmagnetic electrons arise from impurities or are due to a spurious contribution of photoelectrons from the crystal holder has not yet been determined. Note that even in MAG such electrons could be present in addition to the polarized ones, because after all the ESP is not -100%. Maximum B-lattice emission occurs later in LIF, namely at $\hbar\omega \cong 7$ eV, but like in MAG the A-site contribution comes in at higher $\hbar\omega$ than B-site emission, namely from $\hbar\omega = 7.5$ eV on. At $\hbar\omega = 11$ eV, $P = 15\%$, which means that there is already some emission of nonmagnetic electrons in LIF.

Figure 3 shows the photoelectric yield Y (number of photoemitted electrons per incident photon) as a function of $\hbar\omega$ for MAG and LIF. Y is uncorrected for mirror reflectance and window transmission. Above about 8 eV the absolute values are therefore unreliable, but the two curves can still be compared. Using the information from the SSP's, we can understand the Y curves. At low $\hbar\omega$, Y of LIF is smaller. The difference is maximum at $\hbar\omega \cong 7$ eV, where Fe B-site emission is dominant. In LIF, $\frac{1}{2}$ an Fe is missing at the B site, and this is why the yield is lower. On the other hand, Y of LIF is stronger compared with that of MAG at $\hbar\omega \geqslant 10$ eV. This indicates the onset of emission of nonmagnetic electrons in LIF. The thresholds Φ given in Figs. 1 and 2 were evaluated by extrapolating the $Y^{1/2}$-versus-$\hbar\omega$ straight line.

When comparing these results with the one-electron energy diagram proposed by Camphausen, Coey, and Chakraverty[1] for MAG, we see that the data confirm that the d levels are in the band gap between $4s$ and $2p$ bands in contradiction to the results of Balberg and Pankove.[8] Furthermore, the ESP at E_F is negative as predicted in Ref. 1. Important differences are that the nonmagnetic p levels have higher binding energies than proposed and that the centers of gravity of A- and B-site $3d$ levels are not identical. Also, the splitting of $3d$ levels at B sites by the crystal field does not appear. Many of the previous suggestions were based on the fact that Bonnelle[9] found no difference in the soft x-ray spectra of Fe_3O_4 and Fe_2O_3. In the SSP's, the difference is dramatic when Fe^{2+} is missing.

In the present measurement, only the thresholds for emission from different levels are determined, and we can give but an upper limit for the bandwidths. When combining the data of photo-ESP studies with x-ray and uv photoelectron spectra, the widths of the different levels should also emerge.

In conclusion, a direct experimental proof has been given that a down-spin electron from Fe^{2+} at a B site is present at the Fermi energy in MAG. Negative photo-ESP at threshold is also postulated in Ni and Co, but was not detected in the experiment.[10] The present measurements show at least that negative ESP is observed if it exists. Considerable progress is possible with present experimental techniques in understanding the electronic structure of such relatively complex materials as ferrites.

We wish to thank G. Wertheim and M. Campagna for helpful discussions. The encouragement of Professor G. Busch and the financial support by the Schweizerische Nationalfonds are greatly appreciated.

---

[1] D. L. Camphausen, J. M. D. Coey, and B. K. Chakraverty, Phys. Rev. Lett. 29, 657 (1972); N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis Ltd., London, 1974).

[2] J. Smit and H. P. J. Wijn, *Ferrites* (N. V. Philips Gloeilampenfabriken, Eindhoven, Holland, 1962).

[3] U. Buchenau and I. Müller, Solid State Commun. 11, 1291 (1972).

[4] The surface obtained by cleaving was irregular. However, in a magnetic field, one averages over all emission directions, and surface roughness is not important.

[5] D. E. Eastman and J. J. Donelon, Rev. Sci. Instrum. 41, 1648 (1970).

[6] M. Campagna, D. T. Pierce, K. Sattler, and H. C. Siegmann, J. Phys. (Paris), Colloq. 34, C6-87 (1973).

[7] K. Sattler and H. C. Siegmann, Phys. Rev. Lett. 29, 1565 (1972); M. Campagna, K. Sattler, and H. C. Siegmann, in *Magnetism and Magnetic Materials—1973*, edited by C. D. Graham, Jr., and J. J. Rhyne, AIP Conference Proceedings No. 18 (American Institute of Physics, New York, 1974), p. 1388.

[8] I. Balberg and J. I. Pankove, Phys. Rev. Lett. 27, 1371 (1971).

[9] C. Bonnelle, Ann. Phys. (Paris) 1, 439 (1966).

[10] H. Alder, M. Campagna, and H. C. Siegmann, Phys. Rev. B 8, 2075 (1973), and references cited therein.

Virtual Bound States and Configurational Mixing in $Sm_{1-x}Y_xS$ Alloys

T. Penney and F. Holtzberg
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

(Received 25 November 1974)

Resistivity and Hall effect measurements have been made on $Sm_{1-x}Y_xS$ alloys which exhibit black to gold phase transitions as a function of temperature and composition, similar to SmS under pressure. The results indicate that in the gold phase there is a virtual bound state at the Fermi level which causes additional scattering and suppresses the Hall effect. In the black phase, the virtual bound state is below the Fermi level and does not contribute to the Hall effect.

Recently there has been considerable interest in the subject of intermediate valence and valence fluctuations,[1-3] particularly in SmB_6,[4,5] SmS,[6-12] and SmS alloys,[7-9,13-17] in which the Sm f^6 and f^5d configurations are nearly degenerate. In this Letter we report measurements of resistivity and Hall effect in $Sm_{1-x}Y_xS$ alloys which undergo changes in electronic configuration as a function of composition and temperature. This system is of particular interest because the Sm valence can be varied over a considerable range ($\sim$2.0 to $\sim$2.7) at atmospheric pressure. We suggest a model of a virtual bound state of mixed configuration, $(1-\epsilon)f^6+\epsilon f^5d$, which is degenerate with the d conduction band.[18]

SmS is black at zero pressure but collapses to a gold phase under 6.5-kbar pressure.[6] An analogous lattice collapse without external pressure may occur upon alloying SmS with other compounds of smaller lattice constant. The room-temperature lattice-constant data for the $Sm_{1-x}Y_xS$ system shows a discontinuity at $x \approx 0.15$ which divides the system into an expanded "gold" phase. The triangles, Fig. 1(a), demonstrate the unusual lattice expansion on cooling from the gold phase. These data points appear to be continuous with those for samples ($x < 0.15$) which remain black at all temperatures.

Using this lattice-constant data we calculate the valence [Fig. 1(b)] taking the values 6.00 and 5.62 Å for pure divalent and trivalent SmS, respectively.[9] These extrema were obtained by interpola-