Surface Magnetic Hyperfine Interactions in Fe_2O_3 Determined by Energy-Resolved Conversion-Electron Mössbauer Spectroscopy

T. Yang, A. Krishnan, and N. Benczer-Koller
Department of Physics and Astronomy, Rutgers University, New Brunswick, New Jersey 08903

and

G. Bayreuther
Fakultät für Physik, Universität Regensburg, D-8400 Regensburg, West Germany

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The magnetic hyperfine field at ^{57}Fe in uncharacterized Fe_2O_3 films has been measured as a function of depth by a new technique combining high-energy-resolution conversion-electron spectroscopy with Mössbauer resonance absorption. The hyperfine field $H(t)$ was mapped as a function of depth t into the sample. It reaches the bulk value 51.761 ± 0.008 T at a depth of $t_0 \leq 18 \pm 3$ Å below the surface of the film and drops to $H_s \leq 50.6 \pm 0.2$ T at the surface.

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Studies of the magnetic properties of surfaces and interfaces have recently attracted a great deal of attention. Since the existence of magnetically dead layers were reported,[1] there has been no further confirmation. However, extensive studies have revealed either increases or decreases of the magnetization at the interface of metallic iron, metals, or insulators in very thin foils or small grains[2-4] and in multilayered iron metal films sandwiched between thin silver films.[5] Investigations of the magnetic interactions at solid-vacuum interfaces, at surface atoms with adsorbed impurities, or at solid-solid interfaces are essential for the fundamental understanding of exchange interactions in magnetically ordered materials.[6,7]

In this communication we report the first study of the variation of the magnetic hyperfine interaction with depth in an Fe_2O_3 film by a new technique which combines energy-resolved conversion-electron and Mössbauer spectroscopies.[8-10] The Mössbauer resonance is used to excite nuclei distributed uniformly within the sample. The energy spectrum of conversion electrons emitted in the subsequent decay is measured with a high-resolution electron spectrometer. The Mössbauer resonance spectra yield the hyperfine interaction parameters, while the electron energy spectra and electron energy-loss processes relate these parameters to the depth within the sample from which the electrons are emitted.

Semiempirical theoretical models that relate the probability of emission of electrons of a certain energy with their depth of origin provide the means of extracting parameters characterizing the depth. The probability $P(E,t)$ that an electron with a certain energy E within an energy resolution of 2% originates from varying depths t within the sample has been calculated on the basis of a Fermi-age diffusion theory[11] as well as Monte Carlo simulations.[12] We report here an experimental verification of the calculation for the 7.3-keV K conversion electrons emitted in the decay of excited ^{57}Fe nuclei.

The apparatus required for the experiments described below consists of two main components: a velocity transducer and an electrostatic electron spectrometer with an energy resolution $\Delta E/E = 2\%$ and a transmission $T = 13\%$.[13] The absorber containing ^{57}Fe in the appropriate form is placed at the source position of the spectrometer. A 50–100 mCi ^{57}Co (Rh) source located 2 to 3 cm above the absorber and driven by the transducer provides the exciting radiation. At the resonant velocity, the absorber is excited to the 14.4-keV state and subsequently decays by emission of K conversion electrons which are energy selected by the spectrometer. The background of external conversion photoelectrons is measured at off-resonance velocity. The electrons accepted by the spectrometer are emitted within an angle of 75°–90° with respect to the normal to the foil.

Two samples of ^{57}Fe sandwiched between two layers of ^{56}Fe were prepared. The thicknesses of the individual layers were determined to a precision of 2 Å to be ^{56}Fe:^{57}Fe:^{56}Fe = 12:20:150 Å, and 53:15:205 Å, respectively, with the first number referring to the outermost layer. The relative probability of electron emission at a certain energy can be determined either from the net energy spectrum at resonance or from the area under the conversion-electron–Mössbauer spectrum obtained for a particular electron energy. Spectra were obtained at electron energies ranging from 6.5 to 7.2 keV. The relative experimental yields for various electron energies and for different depths of origin were found to be in very good agreement with the Fermi-age model predictions (Fig. 1). Consequently, the model was used to analyze the depth profile of low-energy electrons and to extract the depth dependence of hyperfine parameters.

This study was carried out on hematite (α-Fe_2O_3) films. Hematite is an antiferromagnet with the corundum structure and lattice parameters $a = 5.0345$ Å and $c = 13.749$ Å. The absorber was prepared by evaporation of a 100-μg/cm^2 ^{57}Fe film on a sapphire substrate. The film was then annealed in H_2 at 1000 K for 4 h and oxidized at 1000 K for 4 h. Resonance conversion-electron–Mössbauer spectra emphasizing the two outer lines[14] were obtained for K electron energies ranging from 6.4 to 7.3 keV, and for 5.5-keV *KLL* Auger electrons. All spectra were normalized and subtracted from the spectrum obtained at 7.16 keV, the peak of the K electron line. The difference spectra are a sensitive measure of the difference in hyperfine fields experienced by the nuclei from which the electrons are emitted. The results corresponding to two extreme situations are depicted in Fig. 2: (a) the hyperfine field in the bulk of the material which is probed by 6.85-keV electrons is larger by 0.15% than the field representative of surface layers probed by 7.16-keV electrons; (b) the resonant line obtained for the 7.3-keV electrons which originate from the outermost layers and exit with no energy loss is broader than the line corresponding to the 7.16-keV electrons.

The data were compared with a large set of computer simulations for a variety of hyperfine parameters. Resulting hyperfine-field and linewidth differences were obtained from the best fits to the experimental difference spectra.

The following conclusions can be drawn: (a) The hyperfine field at nuclei near the surface is smaller than at nuclei in deeper layers. (b) The resonance line for the outermost nuclei is broadened by 4%, but the hyperfine field observed for the 7.3-keV electrons is the same as that measured for 7.16-keV electrons. The observed asymmetry in the difference spectrum [Fig. 3(b)] is due to contributions from a 4% background of undegraded K electrons and degraded L electrons from deeper layers for which the hyperfine field is 0.15% larger. (c) The conclusions are corroborated by the spectra obtained for the 5.5-keV Auger electrons. (d) There is no evidence in any of the measurements of changes in either the isomer shift or the quadrupole interactions.

Furthermore, the six-line resonance pattern

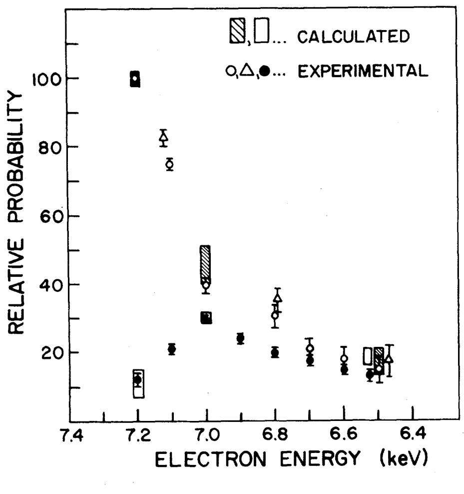

FIG. 1. Relative probability for electrons of initial energy 7.3 keV to exit with a particular energy from a depth t below the surface of an iron foil. For the data represented by open circles (obtained from resonant spectra measured at a particular electron energy) and triangles (obtained from the net electron energy spectrum), t = 12 Å. The filled circles correspond to resonant spectra for t = 53 Å. The square boxes represent the calculations based on the Krakowski and Miller (Ref. 11) model and their height corresponds to an uncertainty of ±1° in the determination of the average electron exit angle from the foil.

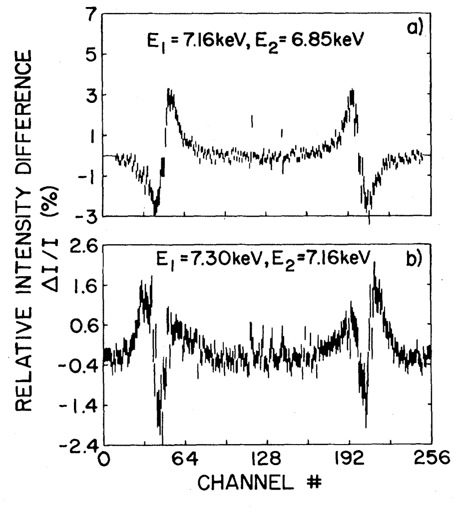

FIG. 2. Difference between the resonant spectra obtained for electrons of two different energies, normalized to the resonant line intensity.

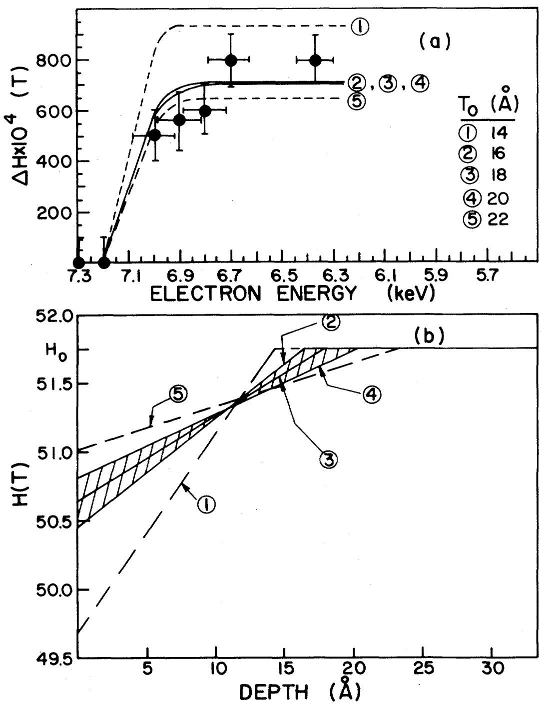

FIG. 3. (a) Experimental mean hyperfine-field difference $\langle \Delta H \rangle = H(E) - H(7.16 \text{ keV})$ obtained from the difference between resonant spectra corresponding to electrons of energy E and 7.16 keV, respectively. The solid and dotted lines correspond to calculations of the hyperfine-field difference assuming that the hyperfine field varies linearly from the maximum bulk value H_0 at a depth t_0 to a lower value H_s at the surface as shown in (b). The solid lines in (a) and the shaded area in (b) display the range of parameters consistent with experimental data.

exhibited the 3:2:1 ratio characteristic of a sample with no preferred alignment. No superparamagnetic peaks were seen near zero velocity indicating that the sample does not contain grains smaller than 500 Å[4]; no additional resonant lines corresponding to Fe bound to impurities were seen either.

The correlation of electron energy with depth was obtained from the calculated[11] probability distributions $P(E,t)$ for iron (see Fig. 5 in Ref. 11). Their results were scaled to account for the differences in the densities of Fe_2O_3 and Fe, and the slightly different electron energy losses in the two materials. The hyperfine field was assumed to vary linearly across the thickness of the sample. On the basis of this assumption, the hyperfine field H at any thickness t can be expressed as

$$H(t) = H_0 + B(t - t_0), \tag{1}$$

where $H_0 = 51.761 \pm 0.008$ T is the bulk magnetic field at room temperature,[15] t_0 is the thickness at which the hyperfine field reaches the bulk value, and B is a constant. The field remains constant at H_0 for thicknesses greater than t_0. The next hyperfine field $H(E)$ determined for electrons of energy E is a weighted sum of the hyperfine fields corresponding to different thicknesses from which the electron emerges with energy E. Thus $H(E)$ can be expressed as

$$H(E) = \int_0^{t_0} P(E,t) H(t)\, dt + \int_{t_0}^{R} P(E,t) H_0\, dt, \tag{2}$$

where R is the range of electrons of energy E. The hyperfine fields $H(E)$ were calculated for various electron energies and compared with experimental values. The parameters t_0 and B were extracted from the simulations that best fit the set of experimental data. Figure 3(a) shows the experimental and calculated differences $\langle \Delta H \rangle = H(E) - H(7.16 \text{ keV})$ of the average hyperfine field for various parameters. The field observed for 6.7- and 6.4-keV conversion-electron energy has saturated to the bulk value. The acceptable values of the parameters describing the hyperfine field should be those that satisfy the conditions that $H = H_0$ for 6.4-keV electrons [shaded area in Fig. 3(b)]. Under the assumption that the surface of the sample is smooth, the analysis of the data yields the thickness t_0 at which the hyperfine field saturates to the bulk value and the average hyperfine field at the surface H_s: $t_0 = 18 \pm 3$ Å, and $H_s = 50.6 \pm 0.2$ T. These results indicate that the surface effects[11] are felt only over a very shallow region. The sample surface may actually exhibit granularity. In this case, both t_0 and H_s obtained from the fits become upper limts: $t_0 \leq 18 \pm 3$ Å and $H_s \leq 50.6 \pm 0.2$ T. In addition, the Fe_2O_3 film surface has not been characterized and might be contaminated with adsorbed or bound H_2, OH^-, H_2O, or other impurities. However, Fe_2O_3 is quite stable chemically. Furthermore, the Mössbauer spectra do not reveal additional lines from contaminants, and neither the isomer shift nor the quadrupole shift indicate binding of Fe nuclei to extraneous impurities. Nevertheless, the observed field reduction at the surface is in qualitative agreement with theoretical predictions[7] of the magnetization profile. These show that the reduction in the magnetization can occur through large depths only for temperatures close to the critical temperature (T_C or T_N). The calculations predict, for example, that for Fe_2O_3 ($T_N = 960$ K) at room temperature, the sublattice magnetization will saturate around two atomic layers below the surface.

The line broadening occurring at the surface coupled with the observation that neither the isomer shift nor the quadrupole interactions change at the surface suggests the existence of a small distribution of either electric field gradients or hyperfine fields at the surface.

In summary, we have presented the first measurement of the variation of the hyperfine magnetic field in iron oxide films down to a depth of 18 Å by means of energy-resolved conversion-electron–Mössbauer spectroscopy. Future studies of the depth profile and temperature dependence of the hyperfine magnetic field will be extended to other magnetic films of accurately characterized surfaces.

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[1] L. N. Lieberman, J. Clinton, D. M. Edwards, and J. Mathon, Phys. Rev. Lett. 25, 232 (1970).

[2] T. Shinjo, J. Phys. (Paris), Colloq. 40, C2-63 (1979).

[3] H. Topsøe, J. A. Dumesic, and S. Mørup, in *Applications of Mössbauer Spectroscopy*, edited by R. L. Cohen (Academic, New York, 1980), Vol. II.

[4] A. M. van der Kraan, Phys. Status Solidi (a) 18, 215 (1973).

[5] S. W. Duncan, R. J. Semper, A. H. Owens, and J. C. Walker, J. Phys. (Paris), Colloq. 41, C1-213 (1980).

[6] D. S. Wang, A. J. Freeman, and H. Krakauer, Phys. Rev. B 24, 1126 (1981).

[7] K. Binder and P. C. Hohenberg, Phys. Rev. B 9, 2194 (1974).

[8] C. J. Song, J. Trooster, and N. Benczer-Koller, Phys. Rev. B 9, 3854 (1974).

[9] U. Bäverstam, C. Bohm, T. Ekdahl, D. Liljequist, and B. Ringström, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman, C. W. Seidel, and D. K. Dieterly (Plenum, New York, 1971), Vol. 9.

[10] W. Jones, J. M. Thomas, R. K. Thorpe, and M. J. Tricker, Appl. Surf. Sci. 1, 338 (1978).

[11] R. A. Krakowski and R. B. Miller, Nucl. Instrum. Methods 100, 93 (1972).

[12] D. Liljequist, Nucl. Instrum. Methods 85, 599 (1981).

[13] T. Yang, B. Kolk, T. Kachnowski, J. Trooster, and N. Benczer-Koller, to be published.

[14] T. Yang, J. Trooster, T. Kachnowski, and N. Benczer-Koller, Hyperfine Interact. 10, 795 (1981).

[15] L. Tobler, W. Kundig, and I. Savic, Hyperfine Interact. 10, 1017 (1981).