SOVIET PHYSICS JETP VOLUME 36, NUMBER 5 MAY, 1973

# MÖSSBAUER-SPECTROSCOPY INVESTIGATION OF THE PROPERTIES OF THIN OXIDE FILMS

I. P. SUZDALEV and A. P. AMULYAVICHUS

Institute of Chemical Physics, USSR Academy of Sciences

Submitted May 31, 1972

Zh. Eksp. Teor. Fiz. **63**, 1758–1763 (November, 1972)

The effective magnetic fields of iron nuclei in thin oxide films on the surface of ultrafine iron particles of 110 ± 20 Å and 240 ± 30 Å diameter were investigated by gamma resonance spectroscopy. The film thickness ranged from 1.5 to 5 monolayers. Nonmagnetic layers on the particle surface were not detected at any film thickness. The dependence of $H_{\text{eff}}$ on the number of layers and the temperature can be satisfactorily described by the spin-wave model with an anisotropy field $H = 10^3-10^4$ Oe. The surface film has an inhomogeneous structure with a large spread of the effective magnetic field strengths. The spread decreases when the temperature is lowered and when an external magnetic field is applied. It is shown that the effective magnetic fields are the same for particles with $d = 110$ and $d = 240$ Å.

STUDY of the magnetic properties of thin films is of great interest for the understanding of the processes whereby magnetic ordering sets in in substances. The existence of nonmagnetic "dead" layers on the surface of magnetically-ordered materials, however, is a question that has not yet been cleared up. Liebermann et al.[1] observed, by measuring the magnetic flux and the magnetization, the existence of nonmagnetic thin films two monolayers thick on the surface of a nonmagnetic material, with magnetization appearing in thicker films. They concluded that there exist two nonmagnetic layers (at zero temperature) on the surface of iron, cobalt, and nickel. Shinjo et al.[2] investigated the magnetic state of a cobalt surface by electrolytically depositing $Co^{57}$ and later using gamma-resonance (Mossbauer) spectroscopy. It turned out that a spectrum with hyperfine magnetic structure (hfs) is observed even for $Co^{57}$ atoms amounting to 0.1 of a monolayer; this shows that the $Co^{57}$ atoms on the surface are in a magnetically ordered state, in contradiction to Liebermann's data. Van der Kraan, likewise using gamma-resonance spectroscopy, investigated the magnetic state of iron on the surface of ultrafine $\alpha$-$Fe_2O_3$ particles with dimension 100 Å. He concluded that the Fe atoms on the surface of the $\alpha$-$Fe_2O_3$ particle are in a magnetic state with a lower effective magnetic field at the nucleus and with a lower Neel point than in the bulk material. Unfortunately, Van der Kraan's conclusions cannot be regarded as unambiguous. Actually, to increase the sensitivity of the method to the state of the surface particles. In such a procedure, the isomorphic replacement of the surface iron ions by $Fe^{57}$ has low probability, and adsorption of the $Fe^{57}$ atoms on the surface is more likely, so that the old surfaces of the $\alpha$-$Fe_2O_3$ particles may not be equivalent to the new surfaces consisting of $Fe^{57}$ atoms.

We have investigated iron oxide films on the surfaces of ultrafine iron particles. This method of investigating surface states of atoms is free of the shortcomings of Van der Kraan's method[3] and, naturally, does not call for deposition of $Fe^{57}$ on the surface, since the spectra of the metallic iron can be easily distinguished from those of the oxide. We investigated the magnetic state of iron-oxide films on the surfaces of particles with diameters 110 ± 20 and 240 ± 30 Å, obtained by an aerosol method described earlier[4]. The particle dimensions were determined with an electron microscope.

The gamma-resonance (GR) spectra of the iron particles with surface oxide films were obtained with a GR spectrometer at constant acceleration of the source ($Co^{57}$ in Cr) at temperatures 80 and 300°K. The isomer shifts were reckoned from the center of hfs of the metallic iron. Some of the spectra were obtained also with a magnetic field of 3 kOe applied to the sample. The oxide-film thicknesses ranged from 1.5 to 5 monolayers and were obtained by oxidation in air at a specified temperature (usually lower than 200°C) and a specified exposure time (up to 1.5 h). The number of atoms on the particle surfaces was estimated from the ratio of the areas under the spectra of the oxide and the metallic iron. A similar procedure was used by us earlier[5, 6]. The number of layers was determined from the number of oxidized iron atoms and from the volume of an oxide monolayer with lattice constant 8 Å.

It is well known[7] that at room temperature there is formed on the surface of metallic iron a layer of $\gamma$-$Fe_2O_3$, which can go over into $Fe_3O_4$ when heated to 200°C. The oxide $\gamma$-$Fe_2O_3$ has a cubic lattice with constant $a = 8.33$ Å. $Fe_3O_4$ has a similar structure with $a = 8.39$ Å, i.e., these structures differ only in that the $Fe_3O_4$ lattice contains divalent iron in comparison with $\gamma$-$Fe_2O_3$. The GR spectrum of $Fe_3O_4$ consists of two hfs systems, and the large effective magnetic field $H_{\text{eff}}$ for one of them is the same as for the hfs lines of $\gamma$-$Fe_2O_3$; we have therefore traced the variation of the larger value of $H_{\text{eff}}$ in the presence of $Fe_3O_4$.

Figure 1 shows the spectra of particles with $d = 110$ and 240 Å, oxidized at room temperature in an external magnetic field $H = 0$ and 3 kOe, and at temperatures 80 and 300° K. Figure 2 shows by way of example the spectra of 110 and 240 Å particles having an oxide film approximately three monolayers thick on the surface (the oxidation temperature and time were 180°C and

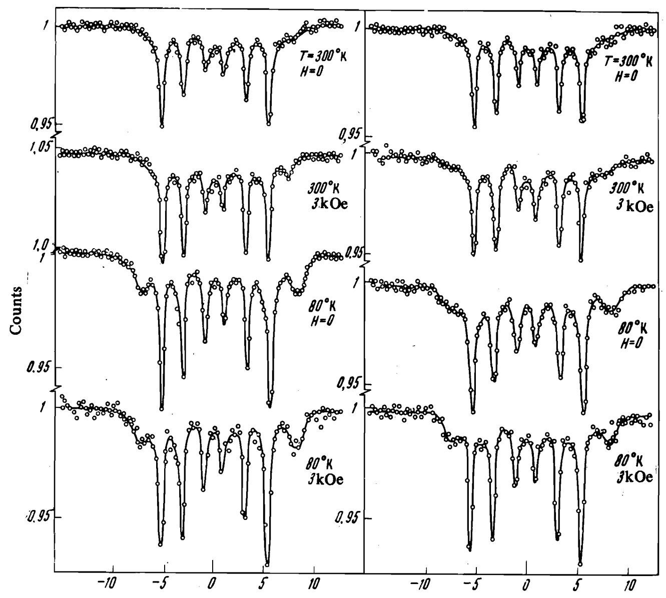

FIG. 1. GR spectra of ultrafine iron particles oxidized at room temperature. Left column—d = 110Å, right column—d = 240Å. The spectra were obtained at different temperatures and in an external magnetic field. The ordinates are calibrated in units of 2 × $10^5$ counts.

1 h, respectively). It is clear from the spectra of Fig. 1 that 1.5–2 layers of the $\gamma$-oxide of iron with magnetic ordering are produced on the particle surfaces. The spectra do not contain the paramagnetic component of iron, so that there are no nonmagnetic "dead" layers on the surfaces of the ultrasmall particles. The effective magnetic field at room temperature is approximately 20% smaller than for bulk $\gamma$-$Fe_2O_3$, and the difference decreases to 7% with decreasing temperature. Application of an external magnetic field $H_{ext}$ = 3 kOe increases $H_{eff}$, just as lowering the temperature does.

We now compare our data with the already mentioned experimental data by others,[1-3], and also with GR-spectroscopy investigations of thin films[8-10]. Lee and Violet[8], Walker[9], and Janot et al.[10] observed vanishing of the magnetic order in thin iron films 5–10 Å thick, deposited on a nonmagnetic substrate, as a function of the temperature. Thus, these additional data[8-10] are likewise in agreement with the results of Liebermann, when it comes to the existence of thin nonmagnetic iron layers on a nonmagnetic material. The situation seems to change radically, however, when the film is deposited on a magnetic material. The existence of even the weak magnetic anisotropy field of the substrate leads to magnetic ordering in the surface film, as was observed by Shinjo et al.[2] and by us with the aid of GR spectroscopy. Indeed, a particle with d ~ 100 Å can produce a magnetic field H ~ $m/d^3$ ~ $10^3$ Oe, where m ~ $N\mu_B$ and N is the number of iron atoms in the particle; this indeed is the cause of the magnetic ordering in the film. A similar effect can be produced by the magnetic field from the neighboring iron particles. Application of a magnetic field $H_{ext}$ = 3 kOe enhances this effect, decreasing the scatter of the magnetic-field directions. There exists thus apparently a certain critical thickness of magnetic-metal film, about two lattice constants. The thickness of the analogous oxide film is unknown. It probably depends strongly on the type of magnetic ordering. There are, however, no nonmagnetic layers on the surfaces of magnetically-ordered bodies, as is unambiguously evident from the results from our experiments.

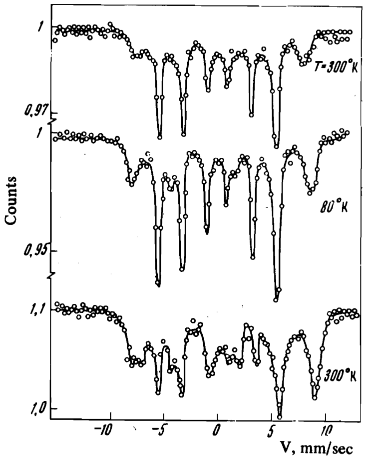

FIG. 2. GR spectra of ultrafine iron particles with oxide film about three layers thick, oxidized at t = 180°C for 1 hour. The two upper spectra correspond to particles with d = 240Å, and the lower to d = 110Å. Unity on the ordinate axis corresponds to 2 × $10^5$ counts.

We turn now to an evaluation of the effective magnetic field in the oxide film, and of its dependence on the temperature and on the applied external field. To this end, we oxidized iron particles in a way that enabled us to observe $H_{eff}$ for films 1.5 to 5 layers thick. There are a number of theoretical models[1,11-14] describing the behavior of the magnetization in thin films as a function of the number of layers and of the temperature. The results of Liebermann et al.[1] pertain to metallic films and are based on Stoner's collectivized model of ferromagnetism. For the oxide film, we attempted to use the molecular-field[11], Heisenberg[12], and spin-wave models[13,14]. The first two models predict that already in the presence of two or three layers the magnetization M differs little from that of the bulk material, thus contradicting the results of our experiment.

As to the spin-wave models developed for thin films, Doring's calculations are more precise and contain the parameter of the magnetic anisotropy field $H_{an}$ produced in our case by the particles. We have therefore used Doring's results[14] in the calculations of $H_{eff}$ = f(T, D), where D is the number of layers and T is the temperature, at different values of the parameter $H_{an}$ = $10^3$–$10^4$ Oe. (We assume $H_{eff}$ = aM throughout.) Doring's theoretical formula[14] is

$$M = N\mu\left[1-\frac{2}{N}\sum_{q}\frac{1}{\exp\{\varepsilon(q)/kT+2\mu H/kT\}-1}\right], \qquad (1)$$

where N is the number of localized electrons with moment $\mu$, and $\epsilon(q)$ is the energy of a spin wave with wave vector q.

Figure 3 shows the results of the experiment and of the theoretical calculations with $H_{an}$ = $10^3$, 4 × $10^3$, and $10^4$ Oe at T = 80 and 300°K for different D. Since the main differences between the values of $H_{eff}$ are observed at room temperature, most experimental points were obtained for this temperature.

It is interesting to note that in spite of the relatively large errors in the determination of $H_{eff}$ and of the

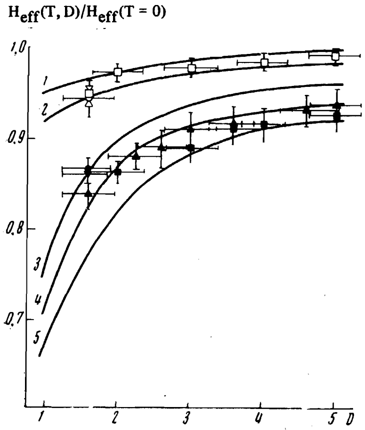

FIG. 3. Experimental values of $H_{eff}$ vs the number of oxide layers on the surface of an ultrasmall iron particle. Dark symbols–300°K, light symbols –80°K, ▲, Δ–d = 240Å, H = 0; ■, □–d = 240Å, H = 0; ▼, ∇–d = 240Å, H = 3 kOe; ●, O–d = 110Å, H = 3 kOe. Solid lines–calculated values of $H_{eff}$: 1–T = 80°K, $H_{an} = 10^4$ Oe, 2–T = 80°K, $H_{an} = 10^3$ Oe; 3–T = 300°K, $H_{an} = 10^4$ Oe, 4–T = 300°K, $H_{an} = 4 \cdot 10^3$ Oe; 5–T = 300°K, $H_{an} = 10^3$ Oe.

number of oxide layers, there is still a noticeable tendency (Fig. 3) for the experimental values of $H_{eff}$ at T = 300°K to go off the theoretical curve for $H_{an} = 4 \times 10^3$ Oe to the curve for $10^3$ Oe. This circumstance is connected with the decrease of the magnetic anisotropy field due to the decrease of the metallic-iron particle through oxidation. We have furthermore investigated particles with different diameters to determine the effect of the particle size on the magnetic properties of the oxide film. The results of the experiments indicate that the oxide films produced on particles with d = 110 and 240 Å have close values of $H_{eff}$. It follows therefore that the particle dimensions and the curvatures of the oxide films do not influence $H_{eff}$ noticeably. The observed fair agreement between the experimental data and the theoretical calculations allow us to conclude that we have observed, by the GR spectroscopy method, the influence of spin waves on the value of $H_{eff}$.

Thus, although magnetic ordering is indeed observed in a thin oxide film on the surface of magnetic material, the values of $H_{eff}$ and M are nevertheless decreased owing to excitation of spin waves at lower temperatures than in bulk samples.

We stop now to discuss one more aspect of the magnetic properties of oxide films on the surface of ultrasmall iron particles. The GR spectra of Figs. 1 and 2 show that the hfs lines of the oxide film are very broad, broader by one order of magnitude than the natural line width. When the temperature is lowered or an external magnetic field is applied, the lines become narrower. Such regularities in the hfs spectra can be due to magnetorelaxation effects in the film. To this end, however, the spin relaxation times of the iron atoms should lie in the range $10^{-7}$–$10^{-10}$ sec if such effects are to appear in the GR spectra. In our case this does not take place. Indeed, although the iron particle with d = 110 Å (when considered in a nonmagnetic environment) is superparamagnetic and the relaxation time of its magnetic moment is close to $10^{-7}$ sec, nevertheless in our case the particles were not insulated from one another, and this could slow down the relaxation and cause the superparamagnetism to vanish[15] because of dipole-dipole interaction. Consequently, the spin relaxation of the iron in the film, due to the superparamagnetism of the particle, cannot lead to a broadening of the lines in the GR spectra.

Another seemingly possible cause of the hfs line broadening in the GR spectrum is the spin relaxation due to spin waves which, as shown above, determine the magnetization and the effective magnetic field in the oxide film. However, the relaxation times for the spin waves amount to $10^{-10}$–$10^{-14}$ sec, i.e., such a relaxation cannot influence the line width in the GR spectrum, and leads only to a certain mean value of M or $H_{eff}$, which we have observed in the experiment. The most probable cause of broadening is therefore apparently the statistical spread of the effective magnetic fields. This spread, which is due to the inhomogeneity of the structure of the thin oxide film, apparently increases with increasing rms displacements of the iron atoms when the temperature is raised[16], and this can also cause the line broadening. Application of an external magnetic field contributes to an increase of the magnetic anisotropy field acting on the film, and decreases the spread in the values of the magnetic fields of the neighboring iron particles. This circumstance leads to a narrowing of the GR spectral lines.

Thus, our investigations have shown that a thin magnetically-ordered oxide film is produced on the surface of ultrasmall iron particles, and there are no nonmagnetic "dead" layers. The film has a highly inhomogeneous structure, resulting in a large magnetic-field scatter that increases with rising temperature. The magnetization and the effective magnetic fields are well described within the framework of the model of spin waves in thin films.

In conclusion, the authors are sincerely grateful to M. Ya. Gen for supplying the samples of highly-dispersed iron and thereby greatly aided the work, to A. M. Afanas'ev for a discussion of the results, and to T. V. Zhuravleva for help with the measurements.

---

[1] L. Liebermann, J. Clinton, D. M. Edwards and J. Mathon, Phys. Rev. Lett. **25**, 232, 1970.

[2] T. Shinjo, T. Matsurawa, T. Takada, S. Nasu and Y. Murakami, Phys. Lett. **36A**, 498, 1971.

[3] A. M. Van der Kraan, Thesis, Krips Repro N. V. Meppel, 1972.

[4] A. M. Afanas'ev, I. P. Suzdalev, M. Ya. Gen, V. I. Gol'danskiĭ, V. P. Korneev, and E. A. Manykin, Zh. Eksp. Teor. Fiz. **58**, 115 (1970) [Sov. Phys.-JETP **31**, 65 (1970)].

[5] I. P. Suzdalev, E. F. Makarov, I. Ya. Garzanov, and L. A. Korytko, Kinetika i kataliz **6**, 1108 (1965).

[6] M. Ya. Gen, I. V. Eremina, V. A. Koltun, E. F. Makarov, V. A. Povitskiĭ, and I. P. Suzdalev, Fiz. Tverd. Tela **9**, 3141 (1967) [Sov. Phys.-Solid State **9**, 2476 (1968)].

[7] Oxidation of Metals (Russ. transl.), J. Benard, ed., Metallurgiya, 1969.

[8] E. L. Lee, P. E. Boldue and U. Violet, Phys. Rev. Lett. **13**, 800, 1964.

[9] I. Walker, Proc. Conf. on the Application of the M. E., Tihan, 1969.

[10] C. Janot, G. Marchal, M. Piecuch, H. Scherrer. C. R. Acad. Sci., Paris, **273B**, 399, 1971.

[11] L. Valenta, Czech. J. Phys. **7**, 127, 133, 1957.

[12] A. Corciovei, J. Phys. Chem. Sol., **20**, 162, 1961.

[13] M. J. Klein and R. S. Smith, Phys. Rev. **81**, 378, 1951.

[14] W. Döring, Z. Naturf., **16a**, 1008, 1146, 1961.

[15] A. Tasaki, S. Tomiyama, S. Iida, N. Wada and R. Kyeda, Jap. J. of Appl. Phys. **4**, 707, 1965.

[16] G. M. Bykov, Zh. Eksp. Teor. Fiz. **44**, 249 (1963) [Sov. Phys.-JETP **17**, 171 (1963)].

Translated by J. G. Adashko
195