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MAGNETIC ORDERING AND CRITICAL THICKNESS OF ULTRATHIN IRON FILMS*

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(Received 15 October 1964)

Early theoretical work[1,2] showed plane nets of atoms to be nonferromagnetic although such arrays in applied fields could result in stable ferromagnetic systems.[3] Experimental investigations,[4-6] which were encouraged by later theoretical work,[7,8] showed that the magnetization decreased relative to bulk value for films which were less than ≈100 lattice parameters thick and appeared to substantiate the spin-wave treatment of Klein and Smith.[7] However, more recent experiments[9-11] have shown that the earlier experimental work was subject to serious error, and that for particles as small and films as thin as 15 Å, the magnetization was essentially equal to bulk value. Thus, the question still remained: At what point does the saturation magnetization show an appreciable thickness dependence?

A major difficulty in thin-film research is the achievement of magnetic saturation for films thinner than ≈20 Å. It occurred to us[12] that the use[13] of the Mössbauer effect in Fe^{57} circumvents this problem and offers a new technique to examine the thickness dependence. We have measured the resonance-absorption spectra of Fe films of 1.2-120Å average thickness at 4.2°K and in the range 298-823°K. Three quantities are derivable from these spectra as a function of film thickness (D) and temperature (T): (1) the magnetic field at the Fe^{57} nucleus $H_n(D, T)$ [$H_n(D, T)$ for bulk Fe^{57} is very nearly proportional to the saturation magnetization $M_S(D, T)$[13,14]]; (2) Curie temperature $T_C(D)$; and (3) quadrupole splitting $2\epsilon(D, T)$ [$=\frac{1}{2}|e^2qQ|$].[15] We conclude from our data that $T_C(D)$ and $2\epsilon(D, T)$, as well as $H_n(D, T)$[$\approx M_S(D, T)$], undergo an abrupt change for films of about two lattice parameters average thickness. This implies the existence of a critical thickness in Fe films.

In order to have enough Fe^{57} to produce observable resonance absorption, samples consisting of alternating layers of Fe (92% Fe^{57}) and SiO were prepared by evaporation in a vacuum system at $\approx 3\times10^{-8}$ Torr. The layers were formed by exposing a quartz cover glass alternately to heated sources containing the Fe and SiO for fixed and reproducible time increments. The SiO evaporation rate was such that the Fe films were separated by 50 Å or more of SiO substrate. The top Fe film was covered with ≈500 Å of Al or SiO. The total Fe thickness was measured by chemical analysis and x-ray emission spectrometry[16] (by far the more accurate). The Fe film thickness was determined by dividing the total Fe thickness by the number of layers. Resonance-absorption spectra were obtained from a Mössbauer spectrometer using a stainless-steel source.[17]

The room-temperature spectra obtained from all samples were of two types: (1) a "six-line" pattern characteristic of the magnetic hyperfine spectrum of metallic iron,[13] and (2) a "two-line" pattern. The six-line spectra were observed only for films of 6 Å or greater thickness; the two-line spectra were obtained only for films of 4.6 Å or smaller thickness. In the six-line spectra, $H_n(D,298°K)$ is essentially equal to bulk value $H_n(\infty,298°K)$ for film thicknesses of 15 Å or greater. For thinner films $H_n(D,298°K)$ decreases slightly and becomes ≈4% less than the room-temperature bulk value at 6 Å. The 6Å film exhibited a quadrupole coupling $\epsilon(6\text{ Å},298°K) = 0.06 \pm 0.02$ mm/sec. No quadrupole coupling was observed in thicker films.

The two-line spectra obtained from films of 1.2-4.6Å thickness consist of two partially resolved lines of equal intensity with a separation of 0.6 mm/sec. The shape of the two-line spectra does not correspond to a collapsed hyperfine pattern.[13] Therefore, $H_n(D, T)$ for films 4.6 Å or thinner must be less than the

excess linewidth, i.e., $H_n < 9$ kOe. We assume the two-line spectra to result from quadrupole splitting of the 14.4-keV Fe^{57} level where ϵ(4.6-1.2 Å,298°K) = 0.3 mm/sec.

All films with the exception of the 4.6Å film yielded essentially the same spectra at 4.2°K as at room temperature. The six-line spectra at 4.2°K show that $H_n(D,4.2°K)$ is 94% of the 4.2°K bulk value in the 7.5Å film and increases to bulk value at 15 Å.

In the 4.6Å film alone, anomalous temperature dependence is observed. This film gives a two-line spectrum at room temperature and a six-line spectrum at 4.2°K. In the temperature range 20-77°K mixed spectra are observed.

In all six-line spectra the intensity ratio is 3:4:1:1:4:3, demonstrating[13] that $H_n(D, T)$ vectors lie in the plane of the substrate. The remarkable uniformity of the Fe films is demonstrated by the facts that (1) with the exception of the 4.6Å film, either a pure six-line or two-line pattern (never an admixture) was observed; and (2) electron micrographs of Fe single films as thin as 25 Å indicate a uniform film with no island formation.

Our data are summarized in Figs. 1 and 2. Curie temperatures have been determined (Fig. 1) from the temperature dependence of $H_n(D, T)$, assuming that the law of corresponding states and the $H_n(\infty, T)$ curve for bulk iron[13] are applicable. There is a large discrepancy between our results and those of previous experimenters (Fig. 2), except for Neugebauer's results,[10] where the agreement is excellent. The room-temperature $M_S(D,298°K)$, as predicted by the molecular field theory of Valenta[18] (MF-V), and the spin-wave theory of Glass and Klein[8] (SW-GK), are also shown in Fig. 2.

The SW-GK theory is plotted for $J = 290k$.[19] This curve can be adjusted to fit our data (for films thicker than two lattice parameters) by assigning an unreasonably large value to J (i.e., $J \approx 6000k$) or limiting the validity of the SW-GK theory to temperatures below 15°K.

Our curves (Fig. 2) for $T_C(D)$ and $M_S(D,298°K)$ agree with MF-V[18] for fcc Fe with (100) orientation in the plane of the film. The values of $T_C(D)$ and $M_S(D, T)$ for the monatomic layer are zero, as predicted by MF-V[18] or spin-wave theory.[1]

In contrast to Fe films, MF-V predicts finite $M_S(D,298°K)$ and $T_C(D)$ for a Ni (bcc) monolayer. The extension of these experiments

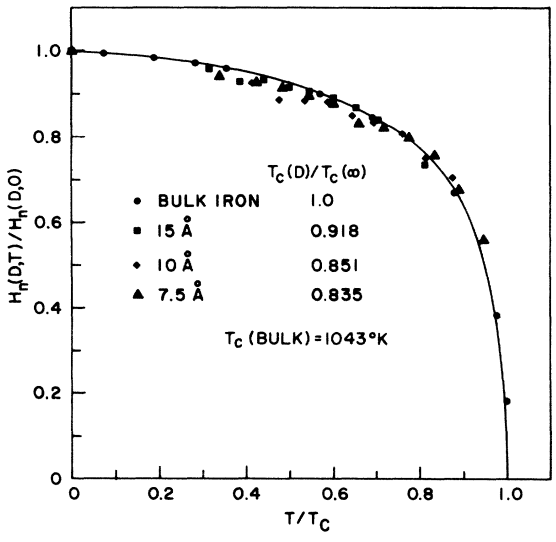

FIG. 1. Relative internal field vs reduced temperature. The observed relative field has been corrected for the substrate effect by the factor $H_n(\infty, 4.2°K)/H_n(D, 4.2°K)$. The curve for bulk iron is taken from reference 13. $T_C(D)/T_C(\infty)$ is the ratio of the Curie temperature for a thin film to that of bulk iron.

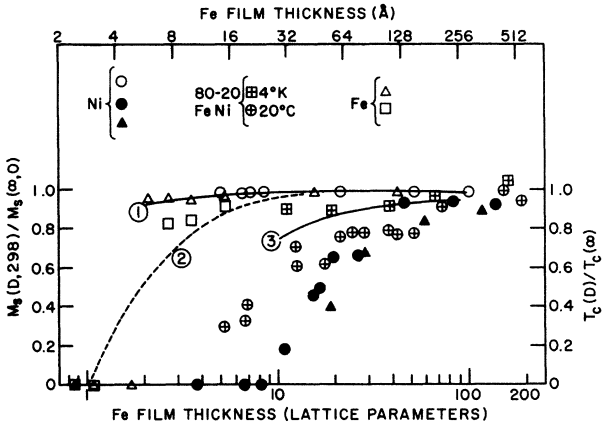

FIG. 2. Relative internal field and Curie temperature vs Fe film thickness. Theoretical values are plotted for a bcc lattice with a (100) direction normal to the film. Previous experimental data on Ni and 80-20 NiFe are also plotted. The difference between the Fe and Ni 80-20 NiFe lattice parameters is neglected. Theoretical: ①, magnetization, MF-V; ②, Curie temperature, MF-V; and ③, magnetization, SW-GK. Experimental: open circle, Neugebauer, magnetization; solid circle, Crittenden and Hoffman, magnetization; solid triangle, Drigo, magnetization; cross in square and cross in circle, Seavey and Tannenwald, magnetization; open triangle, present work, M_S; and square, present work, T_C.

to Ni films is in progress. Experiments using nickel will also have the advantage of allowing a direct observation of T_C since the thin-film samples are stable to approximately 500°C [$T_C(\infty)$ nickel = 358°C].

The assistance of Rex Booth, D. N. Pipkorn, I. Moen, and F. Berting in the conduct of these experiments is gratefully acknowledged.

*This work was performed under the auspices of the U. S. Atomic Energy Commission.

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DILUTE-ALLOY ANTIFERROMAGNETISM IN $Fe_{05}Au_{95}$ †

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(Received 17 November 1964)

The existence of magnetic transition in dilute random-substitutional alloys of Fe in Au has been demonstrated in a number of studies utilizing bulk-magnetization techniques[1-3] and the Mössbauer effect.[4,5] The data have been interpreted in terms of both ferromagnetic ordering and antiferromagnetic ordering. In this Letter we report Mössbauer studies on $Fe_{05}Au_{95}$ as a function of temperature and of an external magnetic field. Our studies show unambiguously that the ordering in this alloy is antiferromagnetic. From Mössbauer polarization measurements we find at temperatures well below the magnetic transition that even in the presence of external magnetic fields of 34 kOe the Fe spin orientation remains almost random, and there is little tendency toward spin orientation either parallel or antiparallel to the external field. Thus the possibility of ferrimagnetic as well as ferromagnetic ordering is excluded for this alloy. We believe this to be the most unambiguous demonstration to date of antiferromagnetism in a dilute random-substitutional alloy.

The magnetic-transition temperature in the Fe-Au system varies almost linearly with concentration for Fe concentrations up to about 15%, thereby indicating the existence of long-range interactions[5] with interaction strength $\sim 1/r^3$. At higher Fe concentrations the transition temperature increases rapidly with Fe concentration as short-range (ferromagnetic) ordering becomes dominant.[2,5] In the linear range the hyperfine magnetic field varies with temperature in a manner similar to that found in metallic Fe.[4] Bulk susceptibility measurements at higher temperature[1,3] follow a Curie-Weiss law and imply a moment per Fe atom