Spin Pinning at Ferrite-Organic Interfaces

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Ultrafine particles of $NiFe_2O_4$ coated with organic molecules show a behavior consistent with extremely strong pinning of the ferrite surface spins. The low-temperature magnetization is only ~ 75% saturated in fields of 200 kOe, and Mössbauer spectra show that the spins remain at large angles with respect to the direction of an applied field of 68.5 kOe. Uncoated ultrafine $NiFe_2O_4$ particles do not show this behavior.

We have previously reported[1] an apparent drastic decrease in the low-temperature moment of ultrafine particles of $NiFe_2O_4$ coated with an organic surfactant such as oleic acid. In this Letter we report Mössbauer and magnetic data which demonstrate that all of the spins are magnetically ordered at low temperatures. Therefore, the apparent loss of moment cannot be due to a magnetic "dead" layer. Furthermore, we present the first evidence for an extremely strong pinning of a large fraction of the spins in the coated particles. Presumably, these pinned spins are associated with those cations on the surface of the $NiFe_2O_4$ particles that are bonded to the organic molecules.

Organic-coated $NiFe_2O_4$ particles were prepared by milling stoichiometric $NiFe_2O_4$ for 1000 h in a mixture of kerosene and either oleic acid or ECA 3852.[2] There was no significant difference in the behavior of particles coated with either of these surfactants. The milled product was centrifuged to remove particles larger than ~ 250 Å diam and washed in methylene chloride to remove excess surfactant. The resulting particles had an average size of ~ 80 Å diam (from electron microscopy and x-ray line broadening) and were coated with 1 or 2 monolayers of the organic molecules (from weight loss on heating). In order to remove all of the organic coating from the particles, they were heated in air at 600°C for 18 h.

An impurity was introduced into the sample as a result of the abrasion of the Fe mill balls and the stainless-steel mill walls.[3] A sample of the impurity was prepared by running the mill without the $NiFe_2O_4$ charge but with all other conditions as described above. Diffraction data for this impurity sample did not indicate crystallinity, and the Mössbauer spectrum was typical of an iron oxide with broadened lines. Magnetic measurements were made on this impurity sample. All magnetic and Mössbauer data reported below have been corrected for the impurity as well as for the weight of the organic coating. The magnitude of the impurity correction was much too small to account for the qualitative features of the observations discussed below.

Magnetic measurements were made in a vibrating-sample magnetometer in fields $\lesssim$ 25 kOe and in a pulsed field apparatus to 205 kOe. Figure 1 shows the corrected moment data obtained at 4.2°K. The top curve was measured on the bulk $NiFe_2O_4$ used to prepare the coated samples. The bottom three curves were obtained on samples of $NiFe_2O_4$ particles coated with oleic acid or ECA. The remaining curve shows the moment of sample *A* after removing the coating by heating in air at 600°C for 18 h. It is apparent from Fig. 1 that the magnetic moments of the coated particles are only ~ 75% saturated at 200 kOe, whereas virtual saturation is achieved in the same field after the coating is removed. The same samples were measured at 77°K in fields up to 205 kOe and had moment values similar to those observed at 4.2°K. The similar values for the high-field moments at 4.2 and 77°K eliminate any possibility of paramagnetic ions.

The same samples were measured at room temperature in maximum fields of only 25 kOe. The data are shown in Fig. 2. The top curve in Fig. 2 is for bulk $NiFe_2O_4$; the bottom three curves are for the coated samples; the middle three curves are for the three samples after the coating was removed by heating at 600°C for 18 h. The gener-

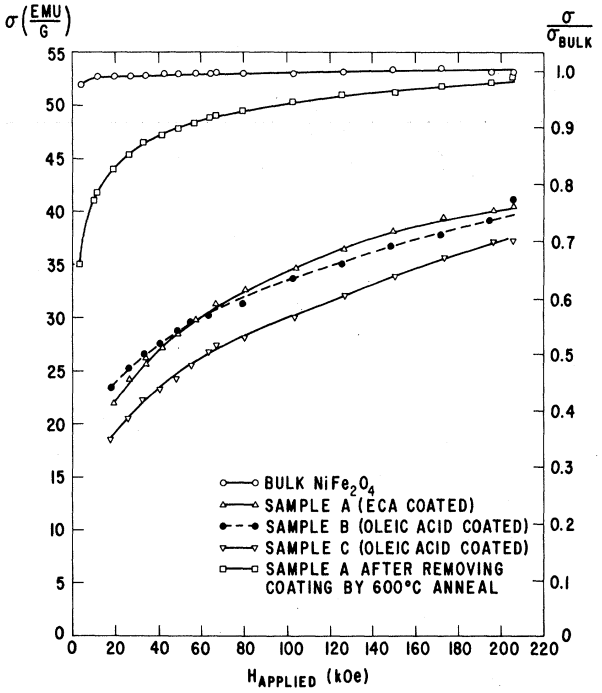

FIG. 1. Magnetization at 4.2°K of bulk $NiFe_2O_4$, coated $NiFe_2O_4$ particles, and a coated sample after removing the coating. Data corrected for mill impurity and weight of organic coating. Low-field data are omitted for clarity of presentation and follow expected behavior for their respective particle sizes.

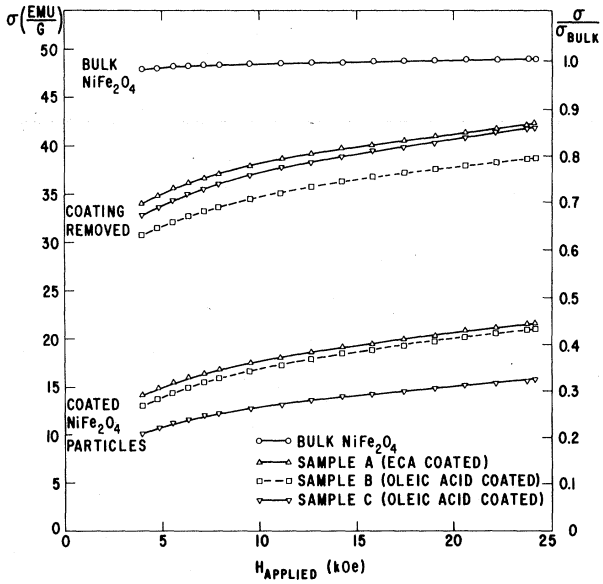

FIG. 2. Magnetization at 295°K of bulk $NiFe_2O_4$, coated particles, and particles after removal of coating. Data corrected for mill impurity and weight of organic coating. Note field scale differs from Fig. 1.

al behavior of the samples at 295°K is the same as at the lower temperatures with allowances for a much lower maximum field. The moments at 25 kOe are < 50% of the bulk moment. After removing the coating, the moment increased markedly. It is extremely unlikely that superparamagnetic behavior[4] is responsible for the low moment of the coated $NiFe_2O_4$ at 295°K in 25 kOe. For $NiFe_2O_4$ particles 80 Å diam in 25 kOe at 295°K, the argument of the Langevin function, mH/kT, exceeds 40, where m is the moment of the particles and k is Boltzmann's constant. These particles would be 98% saturated in 25 kOe at 295°K if they had only the bulk magnetocrystalline anisotropy of $NiFe_2O_4$. Superparamagnetic particles with larger anisotropy would be even more highly saturated. Therefore, it appears that the low magnetization of the coated particles relative to bulk values is a phenomenon that persists at least up to room temperature.

Although these data strongly suggest that the organic coating is responsible for the low measured magnetization, the possibility exists that the low moment is a result only of the small size of the coated particles. Other possible explanations are that the surface morphology or volume strains in the particles might produce anomalous anisotropy or reduced exchange and so result in a lower measured magnetization. All of these features would be eliminated or strongly reduced by the 600°C heating that removed the coating on the particles, and the magnetization would increase. Fortunately, these hypotheses could be tested directly as a group.

Samples were prepared by milling the $NiFe_2O_4$ in alcohol without any surfactant. The resulting particles had closely similar sizes, shapes, and contaminant concentration as the coated particles. Moment measurements were corrected for the mill contaminant by the same method as described above for the coated particles. There was no decrease in measured moment from bulk values for these uncoated particles. In fact, the moment was somewhat higher than for bulk $NiFe_2O_4$.[5] These data confirm that the organic coating on the particles produces the low magnetization.

Figure 3 shows low-temperature Mössbauer spectra taken on bulk $NiFe_2O_4$ and on coated particles of $NiFe_2O_4$. The spectra were taken in zero field and in 68.5 kOe applied parallel to the direction of the γ-ray emission. The spectra for the

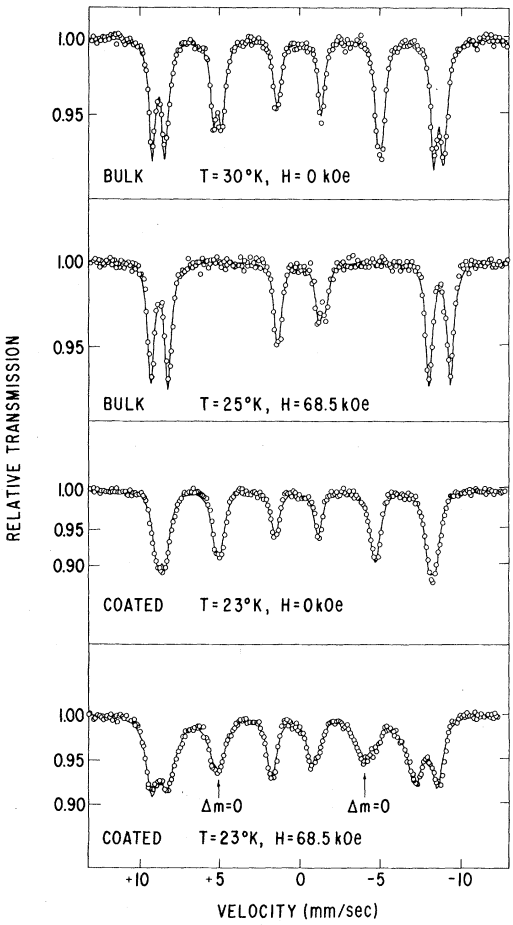

FIG. 3. Mössbauer spectra of bulk $NiFe_2O_4$ and organic coated $NiFe_2O_4$ particles with and without 68.5-kOe field applied collinear with γ-ray emission direction. Mill impurity spectrum subtracted from coated particle spectra. Zero velocity is with respect to Fe metal. A detailed analysis of the line positions with and without a field is given in Ref. 6.

coated samples were corrected by subtracting the spectrum of the impurity measured separately on samples prepared as described above. The major difference between the samples is the vanishing of the $\Delta m = 0$ lines when the field is applied to the bulk sample, whereas this is clearly not the case when the same field is applied to the coated particles. It is important to note that the correction for the impurity can in no way be responsible for the persistence of the $\Delta m = 0$ lines when a field is applied to the coated samples. Furthermore, the sample prepared in alcohol, *without* any organic surfactant, also showed a virtual disappearance of the $\Delta m = 0$ lines in the field. The presence of the $\Delta m = 0$ lines for the coated sample in a field of 68.5 kOe establishes that the hyperfine field is not collinear with the applied field.

The Mössbauer spectra for the bulk $NiFe_2O_4$ were analyzed using a two-sublattice model and neglecting the very small quadrupole splitting. The bulk data both for zero applied field and for the 68.5-kOe applied field are in good agreement with the values reported by Leung *et al.*[6]

The spectra from the coated particles were also analyzed using a two-sublattice model, assuming arbitrary uniform angles φ_A and φ_B between the Fe^{3+} spins in each sublattice and the applied field.[7] The isomer-shift data indicated that the Fe remained in a 3+ state in the coated particles. The analysis also gave $\varphi_A \approx \varphi_B$. We do not have a high degree of confidence in the parameters obtained from this analysis, principally because a uniform two-sublattice model is not likely to be appropriate for the coated particles. However, two things are clear from a *visual* inspection of the coated-particle data: (a) All Fe spins are magnetically ordered (no paramagnetic central peak). (b) The $\Delta m = 0$ lines do *not* vanish in an applied field of 68.5 kOe. If we assume that the A and B sublattices are collinear, i.e., $\varphi_A = \varphi_B = \varphi$, then φ may be readily determined from the ratio $[I_{2,5}(A) + I_{2,5}(B)]/[I_{1,6}(A) + I_{1,6}(B)]$, where $I_{i,7-i}$ are the intensities of paired lines and i gives the line number of the standard six-finger Mössbauer absorption spectrum[7] (the pair 2, 5 corresponds to the $\Delta m = 0$ transition). The value of φ is $46° \pm 10°$ and does not depend on a detailed analysis of the Mössbauer spectrum. From Fig. 1, the fractional magnetization of 68.5 kOe implies a value of $\varphi = 53°$, which is in satisfactory agreement.

Hence the Mössbauer and magnetization data confirm the presence of high effective anisotropy fields in the coated particles.[8] The long-chain surfactant molecules coating the $NiFe_2O_4$ particles are known[9] to adsorb via the action of their polar terminal carboxyl group (–COOH), and it seems plausible that the resulting crystal-field perturbations produce the observed anomalously high effective anisotropy fields. Previous work[1] has indicated that the moment loss is less pronounced in $CoFe_2O_4$ and Fe_3O_4, and we may therefore speculate that the surfactant-ferrite magnetic interaction is especially strongly coupled via the Ni^{2+} ion. A definitive answer must await further investigation.

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[2]Manufactured by Exxon Corp.

[3]T. K. McNab, R. A. Fox, and A. J. Boyle, J. Appl. Phys. 39, 5703 (1968).

[4]E. Kneller, in *Magnetism and Metallurgy,* edited by A. Berkowitz and E. Kneller (Academic, New York, 1969), Chap. 8.

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[8]J. M. D. Coey [Phys. Rev. Lett. 27, 1140 (1971)] has inferred the existence of noncollinear spins in ultrafine particles of precipitated γ-Fe_2O_3. In this case, no organic coating is involved.

[9]R. E. Rosensweig, J. W. Nestor, and R. S. Timmins, in *Proceedings of the Symposium on Chemical Engineering in the Metallurgical Industries, Edinburgh, Scotland, 1963* (Institution of Chemical Engineers, London, 1965), p. 104.

Invariant-Mass Distributions from Inelastic ν and $\bar{\nu}$ Interactions*

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The measured distributions in invariant mass W of the recoiling hadron systems in neutrino- and antineutrino-nucleon inelastic collisions are observed to be significantly different after taking into account the opposite helicities of neutrinos and antineutrinos. These distributions indicate the onset of a new phenomenon in the antineutrino data beginning at an incident energy of about 30 GeV, which appears as an excess of events with $W > 4$ GeV/c^2.

In an earlier paper[1] we presented evidence for a significant difference between the charged-weak-current interactions of neutrinos and antineutrinos with nucleons, distinct from, and in addition to, the difference expected because of the opposite helicities of neutrinos and antineutrinos. Subsequently, we reported other evidence[2] which showed an energy threshold for that effect. Below an energy of about 30 GeV, neutrino and antineutrino interactions were observed to be as expected; above 30 GeV, the difference between neutrino and antineutrino scattering became apparent. In the present paper, with twice the previous data, are given the measured distributions in invariant mass W of the recoiling hadron systems in the neutrino and antineutrino collisions. These distributions also exhibit a distinct difference between neutrino- and antineutrino-induced events, as implied by the scaling-variable distributions from the earlier data,[1] and suggest new particle production by antineutrinos with a mass or masses in the region of 4 GeV/c^2. In addition, they confirm the threshold in antineutrino energy at about 30 GeV.

The experimental method was described in the previous papers[1,2] and also at greater length recently.[3,4] Briefly, an enriched neutrino or antineutrino beam impinged on an ionization calorimeter containing liquid scintillator in which the neutrino-nucleon and antineutrino-nucleon interactions occurred. The total pulse-height output from the calorimeter measured the total energy of the hadron system (E_H) emerging from those interactions. The vector momentum and sign of the electric charge of the outgoing muon were measured in a magnetic spectrometer located directly downstream of the ionization calorimeter. The fractional resolution of the calorimeter,