Magnetic properties of ultrafine iron oxide particles

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The magnetic properties of ultrafine 10–1000 Å iron oxide particles have been investigated by x-ray structural analysis, magnetization measurements, and Mössbauer spectroscopy. A paramagnetic phase is observed in iron oxide x-Fe$_2$O$_3$ for particles smaller than a certain size $d_{cr}=80\pm20$ Å. It is found that d_{cr} depends on the temperature and external magnetic field strength. (d_{cr} decreases with decreasing temperature and upon application of an external magnetic field.) With increase of the dimension ($d > d_{cr}$) the x-Fe$_2$O$_3$ particles change into ferromagnetic γ-Fe$_2$O$_3$. This is accompanied by an increase of the magnetic moment from 0.7 to 40 G cm^{3}g and the appearance of a hyperfine magnetic structure in the γ-resonance spectra. On further growth of the particles, the γ-Fe$_2$O$_3$ phase changes into α-Fe$_2$O$_3$. (This transition occurs for 300–400 Å particles.) The transition from γ-Fe$_2$O$_3$ to the antiferromagnetic phase α-Fe$_2$O$_3$ is accompanied by a decrease of the magnetization from 40 to 2.7 G cm^{3}g. The data are compatible with two interpretations of the phase transition from x-Fe$_2$O$_3$ to γ-Fe$_2$O$_3$. The first is thermodynamic and is based on surface energy, it being assumed that the surface energy of x-Fe$_2$O$_3$ is smaller than that for γ-Fe$_2$O$_3$ whereas the volume energy is greater. In this case the phase transition is due to the intersection of the thermodynamic potential curves for x-Fe$_2$O$_3$ and γ-Fe$_2$O$_3$ at certain d_{cr}. The second interpretation is connected with the assumption of the existence of a first-order magnetic phase transition of the order-disorder type.

INTRODUCTION

The magnetic properties of ultrafine particles of magnetically ordered substances have a number of unique peculiarities, including the phenomenon of superparamagnetism[1], which is due to thermal fluctuations of the magnetic moment of a particle. The relaxation time of the magnetic moment of single-domain, uniformly magnetized particles is given by the expression

$$\tau=\tau_0 e^{Kv/kT}, \qquad (1)$$

where $\tau_0 \sim 10^{-10}$ sec[2].

It is well known that a particle behaves superparamagnetically if the time t necessary for an observation is larger than the relaxation time τ[3]. We note that it is implied here that the particle does not lose its magnetic order in the process of thermal fluctuations. In ordinary magnetic measurements (time of observation $t \sim 1$ sec), an ensemble of superparamagnetic particles is characterized by absence of residual magnetization. When the measurement method used is gamma-resonance (GR) spectroscopy of Fe^{57}, the observation time is $t \sim 10^{-8}$ sec, which is related to the time of Larmor precession of the Fe^{57} nucleus in the magnetic field of the electron spin. In this case, thermal fluctuations of the magnetic moment lead to disappearance of the hyperfine magnetic structure (HFS) in the spectra, accompanied by broadening of the lines and by gradual washing out of them with decrease of the particle dimensions or with increase of temperature[3-24].

Such regularity, however, is not always observed. A number of investigations[8,9,17,18,24] were directed at the magnetic relaxation properties of ultrafine particles of iron oxide with dimensions 50–200 Å, and in all the investigations except[17] the observed spectra differed sharply from spectra with a diffuse HFS system. In references[8,9,18,24], the iron-oxide spectrum consisted of a superposition of a sharp HFS system and a "paramagnetic" part, corresponding to nonmagnetic iron oxide; one part of the spectrum changed to the other upon change of particle dimension and temperature. We remarked earlier[19,20] that such a superposition is at variance with the manifestation of only a single superparamagnetism in the GR spectra. It was suggested that there is a certain critical particle dimension, below which the iron oxide goes over from a superparamagnetic state to a paramagnetic. Then particles with diameter less than a certain d_{cr} give unbroadened spectral lines, corresponding to Fe^{3+} in the paramagnetic state, while those with larger diameter give a spectrum that has a sharp HFS. As is seen from the expression (1), this transition should occur for particles ~100 Å in order that the relaxation time may be longer than 10^{-8} sec and that the superparamagnetism may not lead to a washing out of the HFS lines of the iron oxide. It must be noted that GR spectroscopy can in general not distinguish a superparamagnetic state of the material from a paramagnetic if the relaxation time becomes less than 10^{-10} sec. But this method enables us to set definite bounds to the value of the magnetic anisotropy constant of a superparamagnet, which is related to the relaxation time through formula (1).

On the other hand, by measurement of the magnetization it is usually quite easy to distinguish a superparamagnet from a paramagnet, since the former saturates in small fields ~1–10 kOe. In principle, however, this method also can give only bounds to the value of the magnetic moment per paramagnetic atom in the superparamagnet. It is an important fact that these two methods supplement each other and sharply bound the set of magnetic properties of the material under study; this enables us in most cases to describe the magnetic state of the material quite well.

The present investigation was undertaken with the aim of detecting the transition from the paramagnetic state to the magnetically ordered in ultrafine particles of iron oxide, and of investigating this effect by means of magnetization measurements and GR spectra.

EXPERIMENTAL METHOD AND RESULTS

1. Method of obtaining particles of iron oxide, and data from x-ray structural analysis

The particles of iron oxide were obtained by the topochemical reaction of decomposition of iron oxalate, $Fe_2(C_2O_4)_3 \cdot 5H_2O$, in the temperature range 230—550°C in air. The original salt, in the form of a thin layer, was held for 15 minutes at a given decomposition temperature. As a result, there were obtained 12 particle dimensions from 10—15 Å to 700 Å. The mean particle dimension was determined by adsorption of argon, through measurement of the specific surface. Here[25]

$$d = 6 / \rho S, \tag{2}$$

where ρ is the density of iron oxide and S is the specific surface. The largest surface obtained in our experiments was 250 ± 50 m^2/g; this gave dimension 45 ± 10 Å. It was impossible to determine the specific surface of the particles of smallest dimension because of partial agglomeration of the particles during aging of the specimen in the evacuation process, and also because of the presence of undecomposed iron oxalate.

The particles obtained were studied by x-ray structural analysis. These data indicate that particles with dimensions up to 100 Å give broadened lines, which do not permit an unambiguous comparison of them with one of the phases of Fe_2O_3. (For coarser particles, around 100 Å, there appears a slight admixture of γ-Fe_2O_3.) Particles in the range 100—300 Å consist principally of γ-Fe_2O_3; and, finally, the coarse particles, 300—700 Å, are α-Fe_2O_3.

2. Magnetization measurements

The investigations were made on a vibration magnetometer of the type described by Foner[26]. The magnetic field acting on the specimen could be varied from 0 to 8.5 kOe; magnetization measurements could be made over the temperature range 80—800°K. The sensitivity of the magnetometer was no worse than 10^{-5}. Figure 1 shows results of measurements of the magnetic moment for particles of varying dimension, obtained at room temperature in field 8.5 kOe. Particles with $d_{av} \sim 30$ Å have the value M = 0.7 G cm^3/g, which corresponds to the paramagnetic state of the particles. On increase of the particle dimensions, M increases rapidly, and for particles ~200 Å it reaches 40 G cm^3/g; thereafter it begins to decrease, and for particles ~600 Å it has the value 2.7 G cm^3/g, which is characteristic of α-Fe_2O_3[27]. Figure 2 shows the dependence of M on the value of the magnetic field H applied to the specimen, for particles of various dimensions. Study of the dependence M(H) gives the following. Particles with $d_{av} \sim 30$ Å have a linear dependence of magnetic moment on external magnetic field, as is characteristic of a paramagnet. For particles with larger d_{av}, the dependence M(H) is no longer linear, and a remanent magnetization appears. Particles up to 100 Å must be superparamagnetic; hence it follows that the remanent magnetization observed by us in specimens with $d_{av} < d_{cr}$ indicates an appreciable spread of the particles with respect to dimensions.

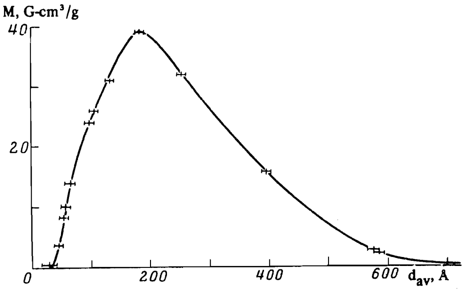

FIG. 1. Dependence of magnetic moment of specimens in field H = 8.5 kOe on their mean dimension (T = 300°K).

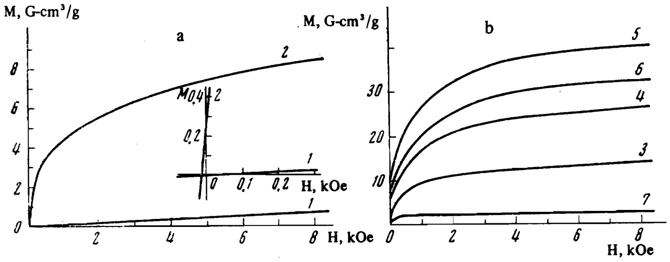

FIG. 2. Dependence of magnetic moment of specimens on field H (T = 300°K): (a) 1, d_{av} = 30 Å; 2, d_{av} = 50 Å; (b) 3, d_{av} = 65; 4, d_{av} = 100; 5, d_{av} = 180; 6, d_{av} = 250; 7, d_{av} = 600 Å.

Thus the results of the magnetization measurements indicate that there is a range of particle dimensions for which the iron oxide is in the paramagnetic state. With increase of the particle dimension above a certain d_{cr}, there occurs a sharp (by two orders) increase of the magnetic moment of the particle, in consequence of its transition to the magnetically ordered state. Because of the fact that the particles have a distribution of dimensions, this transition is smoothed out. Therefore the value of d_{av} will be greater than the particle dimension $d_{av} \approx 30$ Å for which only paramagnetic behavior of M is observed in a magnetic field. It seems expedient to take as d_{cr} the value corresponding to the value of M at the half-height of the curve M(d); this gives $d_{cr} \approx 80$ ± 20 Å. Particles having a mean dimension greater than 80 Å go over to ferromagnetic γ-Fe_2O_3, having a large magnetic moment; this is supported by the x-ray structural analysis. On further growth of the particle, γ-Fe_2O_3 goes over to α-Fe_2O_3, which is antiferromagnetic. This transition is accompanied by decrease of the magnetic moment and is also corroborated by the x-ray structural analysis.

3. Gamma-resonance spectra

In order to study the structure and the magnetic relaxation properties of ultrafine particles of iron oxide, GR spectra were obtained on particles of various diameters from 10—20 to 700 Å. The radiation source was Co^{57} in Cr; the isomeric shifts are reckoned with respect to sodium nitroprussite. Figure 3 shows the GR spectra of particles of various diameters, obtained by room-temperature measurement. The spectra of particles with diameter less than ~60 Å consist of a single doublet with isomeric shift δE_I = 0.53 ± 0.09 mm/sec and with quadrupole-splitting value ΔE_Q = 0.90 ± 0.09 mm/sec. With increase of particle dimension, a hyperfine magnetic structure begins to appear, with magnetic field at the nucleus H_n = 505 ± 5 kOe, corresponding to γ-Fe_2O_3. Here δE_I = 0.53 ± 0.09 mm/sec

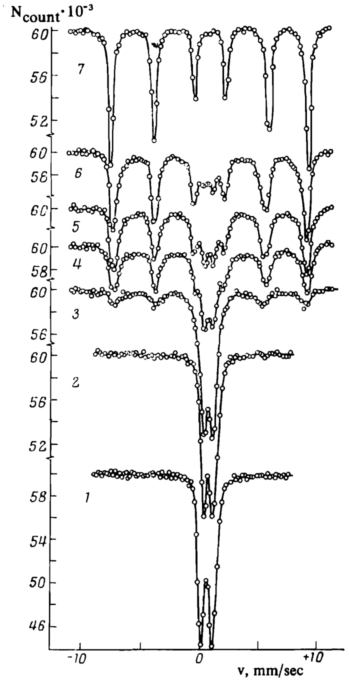

FIG. 3. Mössbauer spectra of specimens (T = 300°K): 1, $d_{av} = 30$; 2, $d_{av} = 50$; 3, $d_{av} = 65$; 4, $d_{av} = 100$; 5, $d_{av} = 180$; 6, $d_{av} = 250$; 7, $d_{av} = 600$ Å (N_{count} = number of counts).

and $\Delta E_Q = 0$. At the same time, with growth of the particles the value of ΔE_Q for the central doublet decreases to 0.63 ± 0.09 mm/sec.

In the range 60—300 Å, the HFS increases its intensity with growth of the particles, but the values of the parameters H_n, δE_I, and ΔE_Q remain essentially unchanged. On further increase of particle diameter (above 300 Å), α-Fe_2O_3 appears, with values $H_n = 517 \pm 5$ kOe, $\delta E_I = 0.62 \pm 0.09$ mm/sec, and $\Delta E_Q = 0.18 \pm 0.09$ mm/sec. The GR spectroscopy data on the ranges of existence of γ-Fe_2O_3 and α-Fe_2O_3 are corroborated by the x-ray structural analysis and the magnetic measurements.

Analysis of the spectra of the specimens at T = 80°K indicates that the spectral parameters of the paramagnetic phase and of γ-Fe_2O_3 remain essentially unchanged, but the intensity of the HFS of γ-Fe_2O_3 increases by comparison with room temperature, with simultaneous decrease of the intensity of the central paramagnetic component.

Application of an external magnetic field, like lowering of temperature, leads to increase of intensity of the HFS and to decrease of intensity of the central component.

Mössbauer measurements for particles ~600 Å, belonging to the α-Fe_2O_3 phase, were made at T = 80 and 300°K; they demonstrated the existence of the Morin transition in particles of this dimension.

On summarizing the results obtained by gamma resonance spectroscopy, we arrive at the conclusion that in these spectra there is no line broadening and washing out of the spectrum as a result of the superparamagnetism, but an unbroadened paramagnetic component goes over to a sharp HFS, corresponding to γ-Fe_2O_3. A similar effect is observed on lowering of the temperature, increase of the particle dimensions, and application of an external magnetic field. This all supports the conclusion that there exists a critical dimension for iron-oxide particles: particles of larger dimensions are in a magnetically ordered state; of smaller, in a paramagnetic.

Thus the data from x-ray structural analysis, the magnetic measurements, and the GR spectra enable us to identify unambiguously the appearance of γ-Fe_2O_3 and its transition to α-Fe_2O_3. But the problem of the structure of the paramagnetic phase remains open. The x-ray structural analysis gives for this phase broadened lines, located at the positions of the γ-Fe_2O_3 and α-Fe_2O_3 reflections; this shows that this phase is crystalline and not amorphous, but it is difficult to determine the type of lattice. On the basis of the GR spectra, it can be concluded that the lattice of this paramagnetic phase—we shall call it the "x"-Fe_2O_3 phase—is strongly distorted; this leads to the large value $\Delta E_Q = 0.63$—0.90 mm/sec. The largest value of ΔE_Q corresponds to the smallest particles and is probably due to the influence of the surface, for which ΔE_Q increases[28].

DISCUSSION OF EXPERIMENTAL DATA

The totality of our experimental data can obviously not be explained by the phenomenon of superparamagnetism alone.

First, as has already been mentioned in the Introduction, superparamagnetic particles with the usual distribution of dimensions, and therefore of relaxation times, cannot give such Mössbauer spectra. In our spectra there is a clearly apparent division of the particles into two groups: those with small relaxation times ($\tau < 10^{-10}$), which give a clearly expressed paramagnetic doublet, and those with larger ones ($\tau > 10^{-8}$), which give six lines. It is also clearly apparent that with change of temperature and of particle dimensions, particles change from one group to the other. With increase of dimensions and lowering of temperature, part of the particles change from the group with small relaxation time to the group with large. A similar effect is observed on application of a magnetic field.

A second important fact is that particles with $\tau < 10^{-10}$ sec have a spectrum with quadrupole splitting $\Delta E_Q = 0.63$ to 0.90 mm/sec, but upon change to the group with $\tau > 10^{-8}$ sec their quadrupole splitting disappears, $\Delta E_Q = 0$.

Third, the data from magnetic measurements are also not compatible with mere superparamagnetic behavior of the particles. The specimen with the smallest d_{av} (≈30 Å) satisfies a linear dependence of the magnetic moment on field H up to fields of 8.5 kOe. All subsequent specimens, with larger d_{av}, have a nonlinear dependence of the magnetic moment on field H; the appearance of nonlinearity is accompanied by the appearance of magnetic hysteresis, which increases with increase of d_{av}. An important fact is that hysteresis is already observed in those specimens in which the Mössbauer spectra still have only a single paramagnetic component.

To explain such anomalies, we have proposed the following interpretation. Consider an isolated particle. Up to diameter $d = d_{cr}$ it is in a paramagnetic state, with the crystal structure of the phase x-Fe_2O_3. At $d = d_{cr}$ it has a discontinuity of magnetization, and above d_{cr} the particle is in a magnetically ordered state, with the crystal structure of the phase γ-Fe_2O_3. It is important that the dimension d_{cr} depends on temperature and on the value of the external magnetic field. The reason for the absence of a discontinuity in a measurement of the total magnetization of the specimen is the presence of a distribution of particle dimensions.

Thus we are suggesting that at the point $d = d_{cr}(T, H)$ there occurs a magnetic phase transition of the first kind, since there is a discontinuity of the first derivative of the thermodynamic potential, $\partial\Phi/\partial H = M$. It is important that the transition is a transition of the first kind both for increase of the particle dimension d and also for change of the temperature and for application of a field H. A second important feature is its reversibility: the reverse transitions occur at the same values of H, d, and T as do the direct. This transition may be either a simple consequence of a crystallographic phase transition, or a peculiarly magnetic phase transition of the first kind. In view of the absence of additional data, solution of this problem does not seem possible at present, and therefore we shall discuss both these mechanisms.

1. Crystallographic phase transition

Consider two phases: the paramagnetic phase x-Fe_2O_3, and the magnetically ordered phase γ-Fe_2O_3. Since the particles are very small, surface energy will play a large role. It is well known[29] that the influence of surface energy leads to formation, at the beginning of crystallization, of metastable phases, which later during the process of growth of a crystalline particle go over to a stable phase. In our case, the thermodynamic potential Φ can be described for each phase in the following form:

$$\Phi_x = \mu_x N + \alpha_x N^{2/3},.$$
$$\Phi_\gamma = \mu_\gamma N + \alpha_\gamma N^{2/3} - \beta HN,$$

where μ is the chemical potential of each phase, α is the surface energy per molecule lying on the surface, N is the number of molecules in the particle, and $N^{2/3}$ is the number of molecules on the surface. In the case of the γ-phase, we have added to the thermodynamic potential a term from the external field. For the x-phase, since it is paramagnetic, this term is small. Here β is the magnetic moment per molecule. Since the magnetic moment per iron atom in γ-Fe_2O_3, determined from the saturation magnetization[30], is $1\mu_B$, it follows that $\beta = 2\mu_B$.

If we suppose that the relations between the values are $\mu_\gamma < \mu_x$ and $\alpha_\gamma > \alpha_x$ (at T = 300°K), then the following situation arises (Fig. 4): up to a certain particle dimension d_{cr}, to which corresponds a definite number of molecules N_{cr}, the thermodynamic potential $\Phi_\gamma > \Phi_x$. Then at the given temperature and for particle dimension $d < d_{cr}$, and consequently $N < N_{cr}$, the particles will be in phase x; for $N > N_{cr}$, in phase γ. If the values of μ_x and μ_γ approach each other on increase of temperature, which is equivalent to the assumption that the phase transition $x \rightarrow \gamma$ in bulk material occurs at a higher temperature (above 300°K), then, as is seen from Fig. 4, on decrease of temperature the point of phase equilibrium N_{cr} shifts in the direction of smaller particle dimension. The same thing happens also on application of an external magnetic field. If we know from experiment the approximate value of N_{cr} ($N_{cr} = 4.9 \cdot 10^3$ molecules for $d_{cr} = 80$ Å) and its shift on application of a magnetic field of 3 kOe, we can determine in order of magnitude $\mu_x - \mu_\gamma$ and $\alpha_\gamma - \alpha_x$.

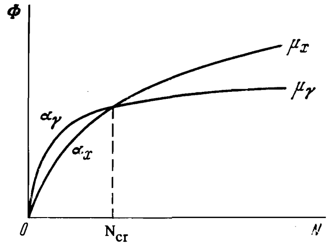

FIG. 4. Thermodynamic potentials of phases x-Fe_2O_3 and γ-Fe_2O_3 as functions of the number of molecules contained in the particle.

On supposing that the shift is 10% (from the change in the relative proportions of the HFS and paramagnetic parts of the spectrum), we get the system of equations

$$N_{cr} = (\alpha_\gamma - \alpha_x)^3 / (\mu_x - \mu_\gamma)^3,$$
$${}^9/_{10} N_{cr} = (\alpha_\gamma - \alpha_x)^3 / (\mu_x - \mu_\gamma + \beta H)^3.$$

Hence $\mu_x - \mu_\gamma \approx 2 \cdot 10^{-15}$ erg/molecule, $\alpha_\gamma - \alpha_x \approx 3 \cdot 10^{-14}$ erg/molecule. Since the absolute values are $\mu \sim 1 \cdot 10^{-11}$ erg/molecule[31] and $\alpha \sim 1 \cdot 10^{-11}$ erg/molecule[32], it is seen that for the γ and x phases the chemical potentials differ only in the fifth significant figure, the surface energies in the fourth.

We have so far considered only the first transition $x \rightleftarrows \gamma$, which is seen directly in the GR spectra. The transition from γ to α can be treated similarly. Since in bulk material the γ-phase is considered metastable with respect to the α-phase, it follows that $\mu_\gamma > \mu_\alpha$.

On supposing that $\alpha_\gamma < \alpha_\alpha$, we get a picture analogous to that just considered. Since γ changes to α in bulk material at 350° C[33], it follows that $\mu_\gamma = \mu_\alpha$ at 350°C. From the mechanism considered above, it is evident that d_{cr} increases with increase of temperature. For particles with $d < d_{cr}$, for arbitrary heating, it is more advantageous to be in the γ phase and not in the α. Particles change to the α-phase with lowering of the temperature. Such a conclusion is compatible with our experimental data. The x-ray structural analysis shows clearly that all α-particles are coarser than γ-particles. The mechanism of transition from γ to α in our case is the following. On increase of temperature the particles sinter, enlarge their dimensions, and thereupon change to the α-phase. The transition evidently occurs at dimensions for which the surface energy is already small in comparison with the volume ($\alpha N^{2/3} \ll \mu N$).

In closing, we note that for such small particles the term "metastable phase" must be applied only to these phases in bulk material, since in our experiments all transitions $x \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ are reversible (for definite particle dimensions).

2. First order magnetic transition

The thermodynamic model presented above describes the experimental data quite well with definite assumptions about the ratios of μ and α for different phases. There are no experimental data on μ and α for different phases of Fe_2O_3; furthermore, we have found no data on a phase of Fe_2O_3 that would be in a paramagnetic state in bulk material and that could be identified with the phase x. Therefore it remains unclear why particles of Fe_2O_3 are in a paramagnetic state up to dimension 80 Å. At the same time, the existence of a paramagnetic phase can be explained as follows.

For this purpose we shall suppose that the phase x has a distorted γ-phase cubic lattice. The distortion is removed when the phase becomes magnetically ordered as a result of a first-order magnetic phase transition. There are quite a few examples of such distorted lattices that come into existence after the disappearance of magnetic order: for example, the occurrence of orthorhombic distortion in the MnAs lattice after a first-order magnetic transformation[34], or the transition to $KFeF_3$, in which a distortion appears in the lattice when magnetic ordering occurs[35].

A qualitative understanding of the possibility of a first-order magnetic phase transition with increase of particle dimensions is possible by use of Blume's model[36], developed by him for a similar transition in UO_2. We assume that the size of the exchange interaction depends significantly on the dimensions of the aggregate, in other words on the particle volume V. The value of the exchange interaction $J = J(V)$ must increase with increase of the dimension and go to saturation with growth of V. It is clear also that saturation must occur at different V for different materials and for different forms of the magnetic ordering. For example, the value of J saturates for γ-Fe_2O_3 at $d \sim 80$ to 100 Å, but for metallic particles of Fe and other materials at $d \sim 10$ to 15 Å, since the saturation magnetization in these particles is unchanged in comparison with the saturation magnetization of bulk material[37-39].

In Blume's model, what is important is the change of $H = \lambda M$, where H is the molecular field, caused by exchange interaction, λ is a constant determined by the exchange-interaction integral, and M is the magnetization. A discontinuity of magnetization occurs when $g\mu_B H = \Delta$, where Δ is the value of the splitting of levels by the crystalline field. How H reaches a given value is mathematically unimportant: whether by increase of $M = M(T)$, as in Blume's own model, or by increase of $\lambda(V) \sim J(V)$, or by increase of H because of addition of an external magnetic field H^{ext}. After H reaches a critical value, there is possible under definite conditions an avalanche-like increase of the magnetization of the specimen, and this is what leads to a first-order magnetic transition.

In our case of the Fe^{3+} ion, the picture becomes significantly more complicated, if only because, when the electronic levels are split by the crystalline field, no nonmagnetic singlet occurs. It is quite possible that in a rigorous solution of this problem it will turn out that only a transition of the second kind can occur. But of the existing theories of first-order magnetic phase transitions of the order-disorder type, the Blume model is the most suitable for explaining our experimental data, and specifically the transition without hysteresis from a nonmagnetic state to a magnetically ordered and back, dependent on T, the particle volume, and the external field.

CONCLUSION

Thus for particles of iron oxide an effect has been discovered, which consists in the existence of a certain critical volume V_{cr} or dimension d_{cr} for the phase x-Fe_2O_3; its value depends on the temperature and on the external magnetic field.

Iron oxide particles having a volume less than V_{cr} are in a paramagnetic state, whereas coarser particles go over to a magnetically ordered state. This effect is characterized by the presence in the GR spectra of two discrete parts, one of which corresponds to the paramagnetic state of iron oxide, the other to the ferromagnetic. It must be noted that GR spectra of this type have been observed also for particles of FeOOH[4,7] and of carbides of the type Fe_2C[13]; this is probably also a consequence of the existence of similar critical dimensions. Apparently the observed effect is not merely characteristic of iron oxide but has a more general character. For observation of it, the critical dimension of the particles must be rather large; otherwise it cannot be detected against the background of superparamagnetism.

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