Size effects in small particles of Fe_3O_4

Yu. F. Krupyanskiĭ and I. P. Suzdalev

Institute of Chemical Physics, USSR Academy of Sciences

(Submitted February 27, 1974)
Zh. Eksp. Teor. Fiz. **67**, 736–743 (August 1974)

By means of gamma-resonance spectroscopy and magnetization measurements, the change of kinetic (conductivity) and magnetic properties of stoichiometric magnetite (Fe_3O_4) with decrease of specimen dimension has been investigated down to 200 Å. "Metal"-dielectric phase transitions have been found on decrease of the specimen dimensions and on application of a magnetic field of 3 kOe. The particle dimension at which the transition occurs (for $T = 300$ K and $H = 0$) is $d = 200$ Å. The results of the magnetization measurements justify the statement that the dielectric ordering in highly dispersed magnetite is significantly different from the Verwey order. An explanation of the existence of such phase transitions is proposed on the basis of the phenomenon of quantization of the energy levels of the carriers on decrease of the particle dimensions to a value $d \lesssim \lambda$ (λ is the wavelength of the current carriers).

INTRODUCTION

Recently much attention has been devoted to the fundamental metal-dielectric problem and to the transition between these states. In this connection, special importance attaches to the comprehensive investigation of substances that possess a rather simple structure and that have been well studied from the experimental and theoretical points of view. One such material is magnetite, Fe_3O_4, in which Verwey observed a transition of this type[1].

As a result of detailed experimental[2–6] and theoretical[7,8] study of magnetite, great success was achieved in explaining the electronic ordering above and below the Verwey temperature. In particular, it was shown[7] that in the conductivity $\sigma = \sigma(T)$ of magnetite at $T > T_V$ the participating carriers are chiefly those with $\lambda \gg c$ (λ = wavelength, c = lattice constant, T_V = Verwey temperature). In this case it is natural to expect a dependence of the kinetic properties of the crystal, in particular of the electrical conductivity, on its dimensions and shape, when the dimensions of the crystalline specimen begin to be comparable with the wavelength of the carriers.

In the present research, by means of gamma-resonance (GR) spectroscopy and magnetization measurements, a detailed investigation was undertaken of the expected changes of magnetic and electric properties of stoichometric magnetite on decrease of the dimensions of the specimen.

In the case of magnetite, the Mössbauer effect provides a unique opportunity to follow the conductivity, since a line structure appears that is characteristic precisely of delocalized carriers. With disappearance of the conductivity (below T_V), this structure disappears. Such a correlation between delocalization and the character of the GR spectra has been reliably established[3–5]. This feature of GR spectroscopy is especially valuable for investigation of small particles, since classical measurements of electrical conductivity on such objects give chiefly information about contact phenomena.

EXPERIMENTAL METHOD AND RESULTS

Magnetite particles were obtained by thermal decomposition of iron oxalate, $Fe_2(C_2O_4)_3 \cdot 5H_2O$, in a deficiency of oxygen. The decomposition temperature was 400°C and higher. The mean dimensions of the particles in the specimens were determined by specific-surface measurements and are given in the figures. For all specimens a careful x-ray structural analysis was made; it justified the statement that all the particles have a composition close to Fe_3O_4, without admixture of α-Fe and FeO. Particles with $d_{av} > 350$ Å have the spinel structure characteristic of magnetite. For particles of the smallest dimension, with $d_{av} = 200$ Å, the x-ray pattern lacks certain lines characteristic of the cubic spinel lattice and contains two lines that cannot be attributed to that lattice. It can be stated that this specimen has a greatly distorted spinel structure, but the resolution does not permit the drawing of an exact conclusion about the lattice structure. An orthorhombic lattice with parameters c = 8.36, a = 5.23, b = 6.05 also fits the results of the analysis within the experimental error.

Figures 1 and 2 show the data of GR spectra for four specimens with different dimensions, for T = 300°K, H = 0 (Fig. 1a); T = 300°K, H = 3 kOe (Fig. 1b); and T = 80°K, H = 0 (Fig. 2). The spectra consist of two systems of hyperfine magnetic structure, corresponding to tetrahedral A sites (lines 1–6) and octahedral B sites (lines 1′–6′) of the iron atoms (lines 4, 4′; 5, 5′; and 6, 6′ of the hyperfine structure coincide). On decrease of the particle dimension, there occurs a change of the ratio of the intensities of the hyperfine-structure lines from A and B sites, manifested in the spectra as a change of the ratio of the intensities of lines 1, 1′; 2, 2′; 3, 3′. A similar redistribution of intensities of these lines, although less marked than with the dimension, occurs on application of an external magnetic field of 3 kOe. The effective fields at the nuclei corresponding to ions in the A and B sublattices at T = 300°K are the same for all specimens:

$$H_{\mathrm{eff}\,(1)} = 490 \pm 5 \text{ kOe}, \quad H_{\mathrm{eff}\,(2)} = 460 \pm 5 \text{ kOe},$$

which corresponds to bulk magnetite[3].

The parameters of the specimen with $d_{av} = 3500$ Å correspond completely to the parameters of stoichiometric bulk magnetite for T = 300°K and T = 80°K[3]. For specimens with smaller dimensions, there appear lines of the hyperfine structure (7, 8, 9) that are not present in bulk magnetite; this may be due either to some imperfection of structure of the particles[9], which is especially characteristic of their surface, or to the appearance of new nonequivalent sites of iron ions.

As is well known[3], the ratio of the intensities of lines in the GR spectra from the A and B sublattices describes the degree of delocalization of the electrons

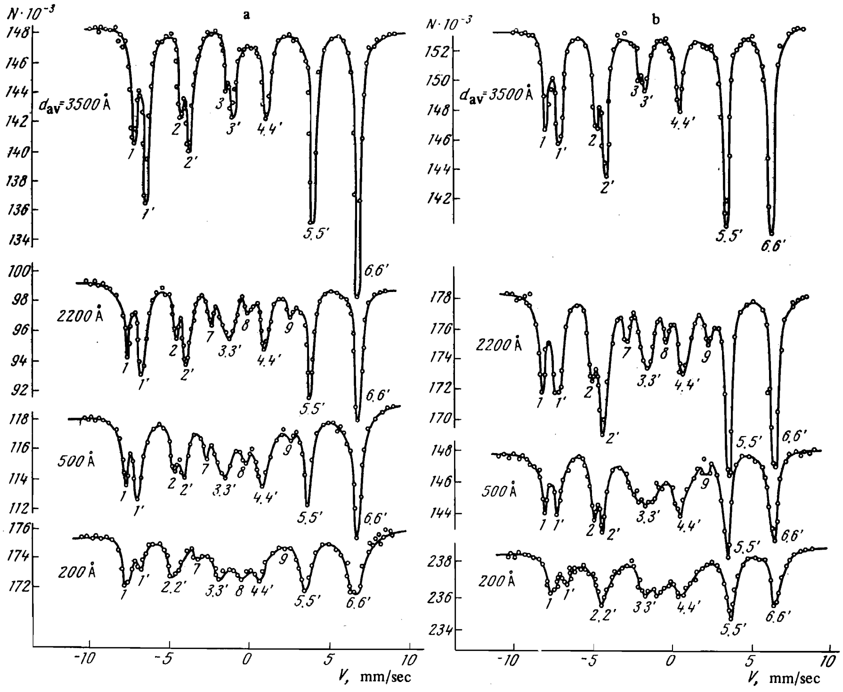


FIG. 1. Gamma-resonance spectra of Fe_3O_4 specimens: a—at T = 300°K and H = 0; b—at T = 300°K and H = 3 kOe.

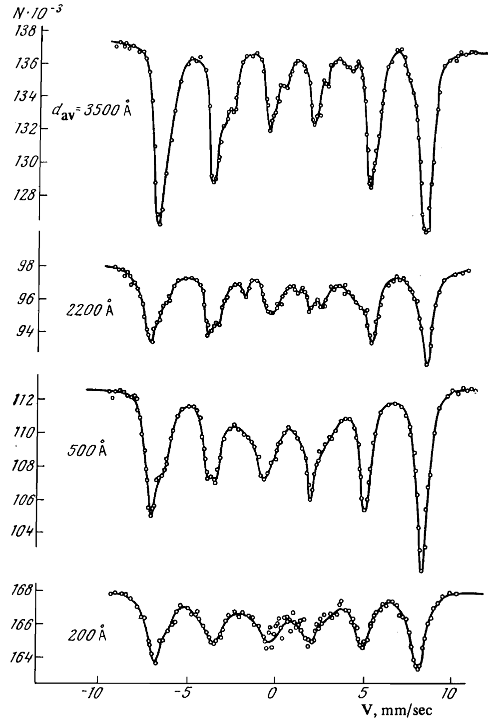


FIG. 2. Gamma-resonance spectra of Fe_3O_4 specimens at T = 80°K and H = 0.

d_{av}, Å	$D = S_{1'}/S_1$ (T = 300 K)	
	H = 0	H = 3 kOe
3500	1.7±0.3	1.6±0.3
2200	1.7±0.3	1.5±0.3
500	1.6±0.3	1.0±0.3
200	0.6±0.2	0.5±0.2

in magnetite, i.e. the degree of "metallicity." We attempt to describe the degree of delocalization by introducing a parameter $D = S_{1'}/S_1$ equal to the ratio of the areas under the lines 1 and 1′ of the hfs spectra. In this case the value D ≈ 2 corresponds to the metallic state and D ≈ 0.5 to the dielectric, as follows from results on measurement of GR spectra and conductivity in bulk specimens[3]. Analysis of the spectra in Fig. 1 gives the following values of D (see the table); this enables us to conclude that with decrease of the particle dimensions, the degree of delocalization decreases, and that for particles with d_{av} = 200 Å the dielectric state of Fe_3O_4 apparently occurs. Application of a weak magnetic field of 3 kOe also promotes localization of the electrons—to a greater degree, the smaller the dimensions of the particle (see Fig. 1b). As is well known, no such effect is observed in bulk magnetite even at rather large fields[3].

The temperature dependence of the hfs was also investigated for particles with d_{av} = 200, 500, 2200, and 3500 Å in the temperature range from 90 to 300°K. Heating above room temperature was not used because of the danger of caking of the particles. The Verwey temperature was determined, by analogy with a bulk specimen, on attainment by the parameter D of a value of order unity[3]. The results of the temperature measurements are shown in Fig. 3, from which it follows that T_V rises with decrease of the particle dimension.

Figure 4 shows the results of a measurement of the saturation magnetization M_S as a function of the particle dimensions. These results correlate quite well with the GR spectroscopy data. When the degree of localization becomes sufficiently large (d_{av} < 700 Å), M_S begins to depart from the value characteristic of bulk material. For d_{av} = 200 Å, i.e. for the dielectric state, M_S(200 Å) is smaller by a factor of about four than M_S for a bulk specimen of magnetite. We note[10,11] that at the Verwey transition in a bulk specimen, M_S decreases suddenly by an amount only of the order of 0.5% of its value.

DISCUSSION OF RESULTS

The totality of the experimental data enables us to state that in small Fe_3O_4 particles a "metal"-dielectric phase transition occurs with decrease of the particle dimensions and application of a magnetic field.

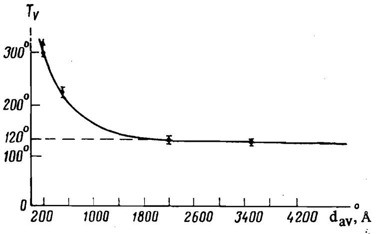


FIG. 3. Dependence of Verwey temperature on dimensions of Fe_3O_4 particles.

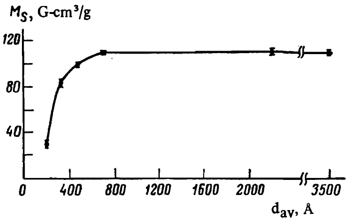


FIG. 4. Dependence of saturation magnetization M_S on mean diameter of specimen particles (T = 300°K).

The question arises, is this effect a purely dimensional effect, or is it a result of the action of other causes?

It is known[1,12] that the Verwey transition is most strongly influenced by astoichiometricity of the specimens, especially on the γ-Fe_2O_3 side. It appears[12] that as little as 4% admixture of γ-Fe_2O_3 leads to absence of the "metal"-dielectric transition. But here the M_S of the astoichiometric magnetite is equal to the M_S of the stoichiometric.

In our research, M_S drops sharply with increase of the localization of the electrons; this in itself rules out astoichiometricity on the γ-Fe_2O_3 side. Furthermore, for example, in particles with d_{av} = 2200 Å there is a Verwey transition, but application of a magnetic field of 3 kOe localizes the electrons to some degree. Consequently, this effect also cannot be due to astoichiometricity of the particles; if in our case the specimens also differ in stoichiometry from magnetite on the side of a surplus of oxygen, it is quite inappreciable ($\ll$ 4%).

Astoichiometricity on the side of α-Fe is easily excluded by the x-ray analysis. Moreover, as shown in[13], it has no influence on the Verwey transition.

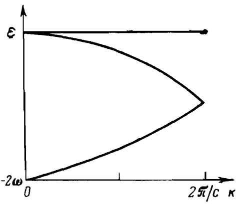
A process of cation redistribution in the process of growth of the particle is also incapable of explaining such effects. According to Néel's theory[14], the magnetic moment of magnetite as a function of the degree of inversion of the spinel is (per molecule)

$$n_\beta = (4+2\gamma)\,\mu_\beta,$$

where γ is the degree of inversion of the spinel. In the case of normal magnetite, γ = 0. For a different cation distribution, within the limits of the spinel structure, M_S can only be larger, whereas in our experiment M_S decreases with decrease of the particle dimension.

The supposition that in this case there is a cation distribution different from the distribution in a spinel, as was suggested in[9], is hardly justified physically, because such exotic compounds have so far not been observed in nature, and the thermodynamic conditions for particles of this dimension differ little from those in bulk material. Furthermore, for such a cation distribution the Verwey transition is completely impossible, whereas in our experiment localization of electrons on application of a magnetic field H is observed in particles that have a Verwey transition.

FIG. 5. Energy as a function of wave vector k, parallel to direction (001), in the "metallic" phase of magnetite [7].



There therefore remains the supposition that these effects are of purely dimensional character. For this there are definite physical prerequisites. In the latest theoretical investigations devoted to the calculation of the conductivity[7] and to the nature of the electronic ordering in magnetite[8], the following band structure is assumed for $T > T_V$ (see Fig. 5). There are two plane degenerate bands and two symmetric bands of width w. Since there are two electrons per elementary cell in magnetite, at T = 0°K the lower bands are filled, and the maximum of the filled bands is at K = 0. In the calculation of the conductivity[7] it is assumed that the lower (valence) band behaves like $|\mathbf{k}|^2$ for small **k**. Since the experimental data are described quite well by theories that use such a dispersion law (and it is correct only for $kc \ll 1$, where c is the lattice constant), it may be assumed that the mobile carriers (holes) have wavelengths $\lambda \gg c$.

When the dimensions of the system, i.e. of the small particle, begin to be comparable with the wavelength of a carrier ($\lambda \gtrsim d$), then quantum effects become important. In particular, if we represent the particle as a three-dimensional square potential well, then between the conduction band and the valence band there begins to arise a gap

$$\Delta E \sim \pi^2\hbar^2/m^* d^2,$$

where m* is the effective mass of the carriers, in general dependent on the system dimension d. This phenomenon in the case of thin films received attention in[15].

As was shown in[16], application of a magnetic field to a specimen possessing semimetal or semiconductor properties leads, under certain conditions, to formation or increase of a gap and to a "metal"-dielectric transition. But while in bulk material the value of the field must be of the order of 10^6 Oe, in particles a slight addition to ΔE can apparently transform the substance from a metal to a dielectric.

The following fact must be noted. In a semimetal of the type of Bi, the value of ΔE becomes of order kT at dimensions $d \sim 10^{-5}$ cm because of the smallness of m*[17]. In the case of a narrow conduction band (large effective mass), characteristic of Fe_3O_4, the mechanism of the "metal"-dielectric transition must be significantly different from the similar transition in semiconductors and semimetals not containing transition elements, though the cause of the transition is evidently the presence of a gap.

A "metal"-dielectric phase transition with respect to dimension or to magnetic field H evidently has, like the Verwey transition, the character of a phase transition of the first kind. This explains the so distorted spinel structure of the particles of the dielectric phase.

We turn now to the data on magnetization measurement. Since in the Verwey transition the saturation magnetization changes very little (~0.5%), whereas in our case it decreases by a factor four on transition from the "metallic" to the dielectric phase, it must be concluded that we have to do with a different character of ordering of the dielectric phase. Apparently in our case noncollinearity of the magnetic sublattices [18] becomes important; this can lead to appreciable antiferromagnetic exchange between Fe^{2+} ions within the B sublattice, and consequently also to decrease of the saturation magnetization.

Thus in the present research, "metal"-dielectric phase transitions have been found experimentally in Fe_3O_4 particles upon decrease of the particle dimension and upon application of a magnetic field. The particle dimension for which the transition occurs at $T = 300°K$ and $H = 0$ is $d = 200$ Å. The experimental data enable us to conclude that the character of the dielectric ordering in the highly dispersed state differs significantly from the Verwey order.

In closing, the authors express their thanks to M. Ya. Kushnarev for performing the x-ray analysis, and to V. I. Gol'danskiĭ and E. F. Makarov for their interest in the research and for valuable discussions.

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Translated by W. F. Brown, Jr.
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