INVESTIGATION OF SUPERPARAMAGNETISM OF FERROMAGNETIC PARTICLES BY MOSSBAUER SPECTROSCOPY

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Submitted August 1, 1969

Zh. Eksp. Teor. Fiz. 58, 115–123 (January, 1970)

A theoretical and experimental investigation of superparamagnetism of ferromagnetic spherical particles is carried out. It is found that the anisotropy energy (relaxation time) drops to zero for crystals with cubic symmetry at particle dimensions of the order of a certain d_{cr}, and then begins to increase with increase of particle size, owing to the turning of the magnetic moments of separate atoms with respect to each other. It is also shown that this phenomenon is not observed in uniaxial crystals. A Mossbauer-spectroscopy investigation of particles of the ferromagnetic alloy FeNi (37% Ni) with a face centered cubic lattice (the particle size varied between 800 and 120 Å) revealed a pronounced anomaly in the hyperfine structure of 190 and 120 Å particle spectra; this confirms the theoretical dependence of anisotropy energy on the particle size.

1. INTRODUCTION

As is well known, the magnetic properties of ferro-, ferri-, and antiferromagnetic substances made of particles of ultrasmall dimensions (on the order of several hundred Å) differ greatly from the properties of the bulky sample, owing to thermal fluctuations of the magnetic moment of each particle as a unit. Although each individual particle remains in a magnetically ordered state, the entire system as a whole behaves like a paramagnet. In the study of this phenomenon, called superparamagnetism, the Mossbauer effect affords unique possibilities of tracing the fluctuations of the magnetic moments of the particles, occurring within relative short times $\sim 10^{-8}$–10^{-9} sec. This question has recently been the subject of a number of investigations in which Mossbauer spectroscopy was used. The greater part of the investigations pertain to antiferro- and ferrimagnetic particles[1-6]. Ferromagnetic particles have been investigated in[7-9].

A theoretical analysis of all the experimental results obtained in these investigations is based on the following notion. In order to reverse the direction of magnetism of the particle, it is necessary to overcome an energy barrier equal to KV, where K is the effective anisotropy energy per unit volume and V is the volume of the particle. Accordingly, the dependence of the time of fluctuation on the particle dimension and on the temperature is determined by the formula

$$\tau = \tau_0 \exp(KV/T), \tag{1}$$

τ_0 is a constant, T is the temperature in energy units. This concept makes it possible to explain qualitatively the obtained experimental results, namely the vanishing of the hyperfine magnetic structure of the Mossbauer spectrum (hfs) with decreasing dimension at a given temperature, and the "effective" lowering of the Curie and Neel points of small-dimension particles.

However, the assemblies of physical phenomena produced in this case are not limited to purely relaxation processes. This pertains primarily to ferromagnetic particles. With changing dimension of the ferromagnetic particle, the magnetic state of the particle itself ranges from the state of homogeneous magnetization in the case of extremely small particles to the domain structure in the case of large particles. This process of realignment of the magnetic structure should obviously exert an appreciable influence on the phenomenon of superparamagnetism and by the same token on the character of the hfs of the Mossbauer spectra.

We report in this paper theoretical and experimental investigations of this problem. As shown by a theoretical analysis, the effective anisotropy constant (the quantity KV in formula (1)) behaves in a nonmonotonic fashion with increasing particle dimension in the case of crystals of cubic symmetry. In the case of spherical particles, KV increases in the interval from zero to d_{cr}, and then decreases rapidly to zero in the interval from d_{cr} to a certain dimension d_1, after which it again begins to increase.

The experiments were performed on spherical particles of FeNi(37% Ni) with cubic symmetry, with dimensions from 120 to 800 Å, and an anomaly in the character of the hfs was indeed observed in the range of dimensions from 120 to 250 Å. In the next two sections we present the results of the theoretical analysis and of the experiment.

2. THEORY

We consider a system of ferromagnetic particles at a temperature below the Curie point, and not subject to the action of an external magnetic field. The total magnetic energy of each individual particle consists of three terms:

$$E = E_{\text{exch}} + E_{\text{md}} + E_{\text{an}}. \tag{2}$$

Here

$$E_{\text{exch}} = +\frac{1}{2}\alpha_{ik}\int \frac{\partial \mathbf{M}}{\partial x_i}\frac{\partial \mathbf{M}}{\partial x_k}d\mathbf{r} \tag{3}$$

is the exchange energy; $\mathbf{M}(\mathbf{r})$ is the magnetic moment

per unit volume of the particle at the point $\mathbf{r}$, and α_{ik} are certain constants.

In crystals of cubic symmetry ($\alpha_{ik} = \alpha\delta_{ik}$) we have

$$E_{md} = -\frac{1}{2}\int\int d\mathbf{r}\,d\mathbf{r}'\,M_i(\mathbf{r})M_k(\mathbf{r}')\frac{\partial^2}{\partial x_i\,\partial x_k}\frac{1}{|\mathbf{r}-\mathbf{r}'|} \equiv \frac{1}{8\pi}\int H^2\,dV \quad (4)$$

is the energy of the magnetic dipole interaction, E_{an} is the energy of the anisotropy, which in the case of crystals of cubic symmetry is determined by the expression

$$E_{an} = K\int (M_x^4 + M_y^4 + M_z^4)\,dV, \quad (5)$$

where K is the anisotropy constant.

In the general case, for particles of not too large dimensions, the distribution of the direction of the density of the magnetic moment $\mathbf{M}(\mathbf{r})$ over the sample of the particle will be determined by the competition between the exchange and magnetic-dipole energies. The magnetic-anisotropy energy, as a rule, is small and can be neglected in the determination of the distribution of $\mathbf{M}(\mathbf{r})$.

We shall stop to consider particles of spherical shape, which are of greatest interest to us. If the radius of the particle is $R \leq R_{cr}$, where R_{cr} is a certain critical radius, then the particle is in the state of homogeneous magnetization, i.e., $\mathbf{M}(\mathbf{r}) = \mathbf{M}_0$ over the entire volume. When $R > R_{cr}$, the state of homogeneous magnetization is no longer energetically most convenient, owing to the presence of E_{md}, and a certain realignment of the directions of the vector $\mathbf{M}(\mathbf{r})$ over the volume of the particle takes place. The problem of finding first R_{cr} was first solved in[10], where it was shown that

$$R_{cr} = \lambda_0\sqrt{3a/4\pi}. \quad (6)$$

It was shown in the same paper that near the critical dimension

$$R - R_{cr} \ll R_{cr} \quad (7)$$

the distribution of the magnetic moment over the sample is given by

$$M_x = -M_0\sin\omega\sin\varphi, \quad M_y = M_0\sin\omega\cos\varphi, \quad M_z = M_0\cos\omega, \quad (8)$$

where $\omega = \omega(r, \theta)$. Here r, θ, φ are the spherical coordinates of the point $\mathbf{r}$.

In addition, in the region (7) we have $\omega(r, \theta) = Cf(r/R)\sin\theta$

$$f(z) = \frac{1}{\sqrt{z}}J_{3/2}(\lambda_0 z) \quad (z = r/R), \quad (9)$$

where $\lambda_0 = 2.085$ is the first root of the equation

$$f'(z) = 0|_{z=1}.$$

Using now formulas (8) and (9) for the sum of the exchange and magnetic-dipole energies, we obtain, accurate to terms of fourth order in C,

$$E_{exch} + E_{md} = \frac{1}{2}M_0^2V\left(\left(\frac{4\pi}{3}\right)^2 + \beta C^2 + \gamma C^4\right), \quad (10)$$

where

$$\beta = 0{,}42\,(R_{cl}^2/R^2 - 1), \quad \gamma = 0{,}0235 - 0{,}0088\,R^2/R^2. \quad (11)$$

(The calculations of the coefficients β and γ are straightforward but rather cumbersome; they are given in the Appendix.)

As follows from (11), when $R < R_{cr}$ expression (10) is essentially positive, and the energy minimum corresponds to $C \equiv 0$. When $R > R_{cr}$, the minimum occurs at

$$C = \sqrt{-\beta/2\gamma}. \quad (12)$$

We now proceed to calculate the anisotropy energy (5). Using (8), we get

$$E_{an} = K(n_x^4 + n^4 + n_z^4)\int(\cos^4\omega - 3\cos^2\omega\sin^2\omega + {}^3/_8\sin^4\omega)\,dV \quad (13)$$

(Here $n = M(0)/M(0)$), and for the potential barrier we get

$$U = \frac{K}{2}\int\left(\cos^4\omega - 3\cos^2\omega\sin^2\omega + \frac{3}{8}\sin^4\omega\right)dV. \quad (14)$$

Let us consider the case when $\omega \ll 1$. Retaining in (14) only the terms quadratic in ω, we get

$$U = \frac{K}{2}\int(1 - 5\omega^2)\,dV. \quad (15)$$

If we compare this expression with the expression for the total moment of the particle

$$M = M_0\int\cos\omega\,dV \approx M_0\int(1 - \omega^2/2)\,dV, \quad (16)$$

then we arrive at a rather interesting result. Indeed, according to (15), given a small deviation of the distribution of $\mathbf{M}(\mathbf{r})$ from a uniform distribution gives an appreciable decrease (larger by one order of magnitude than the relative change of the moment of the particle as a whole) of the effective anisotropy energy, and by the same token, an appreciable change of the effective potential barrier.

Figure 1 shows the dependence of U on the particle dimension (curve 1) in the region from zero to $2d_{cr}$. In this region of dimensions, the deviation from uniform magnetization is still small ($\omega \ll 1$), so that expressions (8) and (14) can be used. As is evident from Fig. 1, the effective barrier changes very sharply in this case, and even passes through zero. This result gives grounds for expecting a sharp change in the character of the hfs of the Mossbauer spectra near the critical dimension in the case of spherical particles of cubic symmetry. We note that such a strong change of U near d_{cr} is not a general rule. Thus, for example, in the case of uniaxial crystals, with easy-magnetization axis along the crystal axis, the change of U no longer has such a strong anomaly in the region $d \sim d_{cr}$. Figure 1 (curve 2) shows the corresponding dependence for spherical particles under the assumption that the exchange energy is determined by formula (1) with $\alpha_{ik} = \alpha\delta_{ik}$, i.e., it has the same form as in cubic crystals. The effective anisotropy energy is then

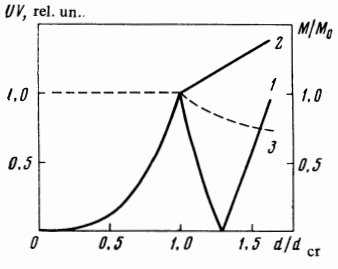

FIG. 1. Calculated dependence of the product of the anisotropy energy by the volume on the diameter of a spherical particle: 1 – crystal of cubic symmetry, 2 – crystal with uniaxial symmetry, 3 – calculated dependence of the relative magnetic moment M/M_0 on the particle diameter.

$$U_{an}^{uniaxial} = \frac{K}{2}\int\left(1-\frac{3}{2}\sin^2\omega\right)dV. \quad (17)$$

It should be noted that in the foregoing analysis the particles were assumed to be strictly spherical. Deviation from spherical form leads to a change in the value of the potential barrier U, which now receives a contribution from the magnetic dipole energy

$$\Delta U \sim \frac{\Delta d}{d} M^2.$$

Figure 1 shows also the decrease of the relative magnetic moment M/M_0 when $d < 2d_{cr}$ (curve 3), which demonstrates clearly the much stronger change of the effective energy of anisotropy for particles having cubic symmetry compared with the change of the magnetic moment.

3. EXPERIMENT

Spherical particles of the alloy FeNi(37% Ni) were obtained by a condensation aerosol method, similar, for example, to that used in[11]. The particle dimension is determined with an electron microscope. Aerosols were obtained with particles of the following dimensions: $d_1 = 800 \pm 80$ Å, $d_2 = 450 \pm 45$ Å, $d_3 = 350 \pm 35$ Å, $d_4 = 250 \pm 25$ Å, $d_5 = 190 \pm 20$ Å, and $d_6 = 120 \pm 20$ Å. The FeNi alloy (37% Ni) was chosen for the investigations because of its low Curie point, ~350°C, and because the composition is single-phase. An x-ray structure analysis has shown the presence of a γ phase (body-centered cubic lattice) in all particles.

The low Curie point makes it possible to observe relaxation processes in the system at relatively low temperatures, excluding a change in the chemical state of the iron. The point is that particles with d equal to 190 and 120 Å experience recoil after the iron nuclei emit γ quanta, and this leads to a vanishing of the Mossbauer effect. Therefore all the samples were prepared by mixing particles of the alloy with heat-resisting resin, capable of with-standing heating up to 400°C. We have noted that at temperatures above 300°C a topochemical reaction sets in between the highly dispersed FeNi alloy and the resin, thereby changing the chemical state of the iron atoms. It was therefore highly desirable to have a system in which one could operate without heating it above 250°C. The alloy with 37% Ni turned out to be such a convenient system for the observation of relaxation effects. The Mossbauer spectra of FeNi particles were obtained using a spectrometer with variable velocity, using a Co^{57} source in Cr. The number of accumulated pulses in each channel was $(4-7)\times 10^5$.

Figure 2 shows the spectra of four different particle dimensions, namely 450, 250, 190 and 120 Å, at different temperatures. The temperature 483°K turned out to be the most convenient for the observation of the relaxation processes in particles with d = 800–250 Å, since the largest difference in the character of the hfs of the spectrum as a function of the particle dimension was observed at this temperature. Unfortunately, at this temperature the particles with d = 190 and 120 Å already produce in the spectrum only one narrow line, and it is impossible to reveal the influence of the dimension on the relaxation of the magnetic moments. Therefore, for the smallest particles we investigated the Mossbauer spectra up to 393°K.

An analysis of the spectra of even the largest particles has shown the presence of superparamagnetism and a dependence of the relaxation time on the particle dimension. At 483°K, with decreasing particle dimension, the hfs of the spectrum becomes much less pronounced and the central "paramagnetic" component increases. A particularly sharp change occurs in the character of the spectra on going over to the smallest particles (190 and 120 Å).

Indeed, the paramagnetism becomes most strongly manifested in the region of temperatures 400–500°K, when the particle diameter becomes of the order of 200–300 Å. Thus, at an isotropy constant $\sim 10^4$ erg/cm^3 (this is characteristic of the FeNi alloy with 37% Ni), these dimensions give a magnetic-moment relaxation frequency $\sim 10^8$ sec^{-1}, which is comparable with the frequency of the Larmor precession of the spin of the Fe nucleus. In this connection a strong difference is expected to exist between the spectra of particles with dimensions 250 and 190 Å. A still greater difference should occur in the spectra of the 190 and 120 Å particles. The analysis of the spectra offers evidence (compare Figs. 2b and c) that a decrease of the particle dimensions from 250 to 180 Å leads to an appreciable decrease of the relaxation time and to an almost complete vanishing of hfs already at 393°K (Fig. 2c), for the particles with d = 190 Å, whereas for the particles with d = 250 Å the hfs begins to disappear only at 483°K.

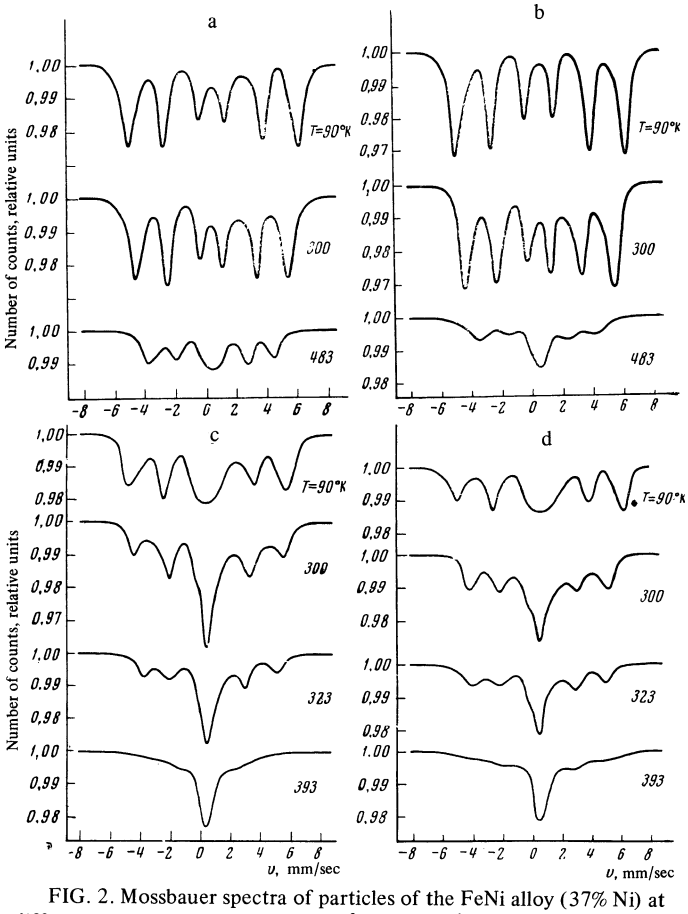

FIG. 2. Mossbauer spectra of particles of the FeNi alloy (37% Ni) at different temperatures: a – d = 450 Å, b – 250 Å, c – 190 Å, d – 120 Å.

Values of $S = I_p/I_{hfs}$ for particles with d = 800–120 Å at different temperatures

d, Å	T, °K				
	483	393	323	300	90
120	—	5.2±0.35	3.5±0.27	2.4±0.27	1.1±0.27
190	—	6.5±0.45	4.4±0.27	3.6±0.27	1.3±0.27
250	2.6±0.35	—	—	—	—
350	2.5±0.35	—	—	—	—
450	1.4±0.27	—	—	—	—
800	1.1±0.27	—	—	—	—

A comparison of the spectra of the particles with d = 190 and 120 Å (Figs. 2c and 2d) shows, however, an unexpected anomaly in the relaxation of the magnetic moment of the particle with d = 120 Å. Instead of revealing a further sharp vanishing of the hfs compared with the spectrum of the particles with d = 190 Å, the spectrum of the particles with d = 120 Å is quite similar to the spectrum, and even has a somewhat larger hfs contribution compared with the "paramagnetic" (central) component than the spectrum of the particles with d = 180 Å. This indicates that the relaxation time of the magnetization in the particle with dimension 120 Å is equal to or even larger than in the particle with dimension 190 Å.

Because of the complexity of the relaxation in the cubic lattice, it is very difficult to estimate the relaxation time. Indeed, the Mossbauer spectra in the region of the investigated temperatures give rather broad lines, the widths of which vary little with temperature and with particle dimension.

There exists, however, another experimental parameter, which is more sensitive to relaxation. This is the ratio of the amplitude of the central "paramagnetic" component of the spectrum to the amplitude of the outermost hfs lines, $S = I_p/I_{hfs}$. The decrease of the relaxation time leads to an increase of this parameter, with the aid of which it is possible to describe clearly the change of the relaxation time of the magnetic moment with decreasing particle dimensions.

The table lists the values of S for 800, 450, 350, and 250 Å particles, obtained from the particle spectra at T = 483°K, and for the 190 and 120 Å particles at temperatures 90, 300, 323, and 393°K. S has a maximum at 190 Å, characterizing the fact that when the particle dimension decreases to 190 Å the relaxation time decreases, and then, at 120 Å, it again increases.

4. DISCUSSION OF RESULTS

The experimental and theoretical investigations have shown that for ferromagnetic spherical particles having cubic symmetry of the crystal lattice, in the vicinity of critical dimensions, where realignment of the distribution of the magnetic moment takes place, there is an abrupt change in the relaxation time of the magnetic moments. This leads to an anomalous dependence on the character of the hfs on the particle dimension.

The observed phenomenon is quite unexpected and is of independent interest. On the other hand, this makes it possible to determine experimentally the critical dimension of the particle, to obtain information concerning the exchange interaction in ferromagnets. The obtained results cannot as yet be compared quantitatively with the theoretical calculations, since in the region $R \sim R_{cr}$ we had only two particle dimensions. It is therefore necessary to have a denser particle distribution in this range of dimensions. The corresponding investigations are being continued.

In conclusion, we are grateful to Yu. F. Krupyanskiĭ for help in preparing the samples and to I. V. Plate for the x-ray structural analysis.

APPENDIX

If the distribution of the magnetic moment over the sample is given by formula (8), then the expression (3) for the exchange energy (with $\alpha_{ik} = \alpha\delta_{ik}$) can be readily reduced to the form

$$E_{exch} = \frac{1}{2}\alpha M_0^2 \int_V \left[\left(\frac{\partial\omega}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial\omega}{\partial\theta}\right)^2 + \frac{\sin^2\omega}{r_i^2\sin^2\theta}\right] dV. \quad (A.1)$$

Using for $\omega(r, \theta)$ the expression (9) and confining ourselves to terms up to fourth order in ω, we readily get

$$E_{exch} = {}^1/_2 M_0^2 V(\beta_1 C^2 + \gamma_1 C^4), \quad (A.2)$$

$$\beta_1 = \frac{8\pi}{3}\frac{R_{кр}^2}{R^2}\int_0^1 z^2 f^2(z)\,dz, \quad \gamma_1 = -\frac{8\pi}{9}\frac{R_{кр}^2}{R^2}\int_0^1 f^4(z)\,dz. \quad (A.3)$$

The expression for the magnetic dipole energy (4) is best rewritten in the form

$$E_{md} = \frac{1}{2}\int\int dr\,dr' \frac{\operatorname{div}\mathbf{M}\operatorname{div}\mathbf{M}'}{|\mathbf{r}-\mathbf{r}'|} - \int\oint dr \frac{\operatorname{div}\mathbf{M}(\mathbf{M}'\,dS')}{|\mathbf{r}-\mathbf{r}'|} + \frac{1}{2}\oint\oint \frac{(\mathbf{M}\,dS)(\mathbf{M}'\,dS')}{|\mathbf{r}-\mathbf{r}'|}. \quad (A.4)$$

Substituting in (A.4) formulas (8) and (9), and confining ourselves to terms of fourth power in ω, we obtain by direct integration an expression of the type (A.2) for E_{md}:

$$E_{md} = \frac{1}{2}M_0^2 V\left\{\left(\frac{4\pi}{3}\right)^2 + \beta_2 C^2 + \gamma^2 C^4 \right. \quad (A.5)$$

With coefficients

$$\beta_2 = -\frac{8\pi}{3}\int_0^1 z^2 f^2(z)\,dz,$$

$$\gamma_2 = \frac{8\pi}{3}\frac{16}{105}\int_0^1 z^2 f^4(z)\,dz \quad (A.6)$$

$$+ 54\pi\int_0^1 dz\int_0^z dz_1 f^2(z) f^2(z_1)\left\{\frac{1}{2}\left(\frac{4}{15}\right)^2\frac{r_1^2}{r} + \frac{2}{9}\left(\frac{4}{35}\right)^2\frac{r_1^4}{r^3}\right\}.$$

Numerical integration of (A.3) and (A.6) then leads to the result (11).

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Translated by J. G. Adashko
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