ON THE THEORY OF THE INFLUENCE OF FERROMAGNETIC PARTICLES ON EPR SPECTRA OF DIELECTRICS

Ya. G. DORFMAN

All-union Institute of Scientific and Technical Information

Submitted to JETP editor August 26, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 48, 715-718 (February, 1965)

We investigate theoretically the influence of dispersed ferromagnetic inclusions on the epr spectrum of a dielectric that contains individual unpaired spins. It is shown that whereas medium and large ferromagnetic particles should give rise to characteristic broad ferromagnetic resonance lines, very minute ferromagnetic particles may produce narrow ferromagnetic resonance lines that seem to simulate the epr lines of individual spins.

It is well known that weakly-magnetic solids frequently contain ferromagnetic impurities in the form of minute solid inclusions.[1,2] Magnetostatic investigations make it possible to observe these impurities in samples containing less than 10^{-4}% of iron, corresponding to 10^{13}—10^{14} unpaired spins per gram of sample. It is natural to expect that the epr method, which is capable of observing 10^{10}—10^{12} spins per gram, should be especially sensitive to ferromagnetic inclusions. This question is of interest because the epr method is widely used at present for the study of various objects, which may contain not only accidentally introduced ferromagnetic contaminations, but also ferromagnetic particles resulting from chemical decomposition of the constituents. Unfortunately, the existing books and reviews on electron paramagnetic resonance do not consider this question, mention it only in passing, and only with respect to metallic objects at that[3]. It is our purpose in the present article to consider this question only as applied to dielectrics, where the phenomena are simpler.

We consider an isotropic solid diamagnetic dielectric, in which there are, besides the individual unpaired spins, randomly distributed particles of a ferromagnet, with distances between them so large that their interaction with one another can be completely neglected. For simplicity we assume that the particles are in the shape of solids of revolution and have uniaxial magnetocrystalline anisotropy, with the axis of rotation not necessarily coinciding with the axis of the magnetic crystalline anisotropy. We assume that the particles are single-domain, as is undoubtedly the case for not too large particles.

We assume further that, in accordance with the latest experimental data[4], the particles are ferromagnetic down to the smallest sizes (with diameter of several Angstroms) at room temperature, and that the saturation magnetization I_0 per cubic centimeter is practically the same for all particles. Each particle can be characterized by an anisotropy constant K that depends both on the anisotropy of the shape and on the anisotropy of the crystal structure. If at a temperature T the anisotropy energy of the particle is $K\bar{v} > kT$ (where $\bar{v}$ is the average volume per particle), then in the absence of an internal magnetic field the vector of spontaneous magnetization $\mathbf{M} = I_0\bar{v}$ is oriented parallel to the anisotropy axis. On the other hand, if $K\bar{v} < kT$, then the direction of the vector $\mathbf{M}$ fluctuates. Therefore the aggregate of particles displays in the former case properties of a normal ferromagnet, and in the latter case it exhibits properties of macroparamagnetism (or superparamagnetism).

This means that in the presence of a sufficiently strong external field H the aggregate of particles of the first type becomes magnetized, reaching a saturation value $J_0 = NI_0\bar{v} = N\overline{M}$ (where N is the number of particles per cubic centimeter of sample). The aggregate of particles of the second type ($K\bar{v} < dT$) exhibits a magnetization

$$J = N\overline{M}\coth\frac{\overline{M}H}{kT} - \frac{kT}{\overline{M}H}, \tag{1}$$

and if $\overline{M}H \ll kT$

$$J = N\overline{M}^2H / 3kT. \tag{2}$$

Superposition of a high-frequency field of frequency ν on the constant magnetic field H should produce ferromagnetic resonance in the ferromagnetic particles, and also electron paramagnetic resonance with the isolated unpaired spins present in the dielectric (free radicals, etc.). The intensity of either effect is proportional to the corresponding magnetization J in the field H. The magnetization N′ of the isolated spins is

$$J' = N'\mu^2 H / kT, \qquad (3)$$

where μ is the Bohr magneton. Inasmuch as $\overline{M} = \bar{n}\mu$, we find that for $N\bar{n} = N'$, that is, when the unpaired spins in the ferromagnetic impurity and in the dielectric are equal in number the intensity of the ferromagnetic resonance line of the particles will be $\approx N'\mu$ when $K\bar{v} > kT$ and $\sim N'\bar{n}\mu^2 H/kT$ when $K\bar{v} < kT$, if $\bar{n}\mu H < kT$, whereas the epr line intensity will be $\approx N'\mu^2 H/kT$.

This means that when $N\bar{n} = N'$ the ferromagnetic resonance lines of the particles will be much more intense than the epr lines of the individual unpaired spins. In the case when $K\bar{v} < kT$, the temperature dependence of the ferromagnetic resonance and of the electron paramagnetic resonance will be practically the same, with the ferromagnetic resonance line intensity of the ferromagnetic particles following approximately the Curie law.

If the anisotropy axes of the ferromagnetic particles are oriented in random fashion and are rigidly fixed, while the width of the ferromagnetic resonance line of each particle is small, then ΔH, the width of the observed ferromagnetic resonance line due to the entire aggregate of particles, is characterized by a scatter of the effective magnetic fields H_{eff} in the particles. Inasmuch as

$$H_{\text{eff}} = H \pm K I_0^{-1} \cos\varphi, \qquad (4)$$

where φ is the angle between the direction of the anisotropy axis of the given particle and the direction of the external field H, we have

$$\Delta H = 2KI_0^{-1}\overline{|\cos\varphi|} = 4K/\pi I_0. \qquad (5)$$

Usually the anisotropy constant of ferromagnetic crystals is $K = 10^4 - 10^5$ erg/cm^3, while $I_0 = 10^2 - 10^3$. Therefore, in the case of nearly spherical particles (that is, in the absence of shape anisotropy), we have $\Delta H \approx 10^2 - 10^3$ Oe. The shape anisotropy is determined by the difference in the coefficients of magnetization of the particle in two mutually perpendicular directions A_1 and A_2. The largest value of $A_1 - A_2$ is $\cong \pi$. In this case $K \cong \pi I_0^2$, meaning again that $\Delta H \cong \pi I_0 \cong 10^2 - 10^3$ Oe. In other words, the ferromagnetic resonance line of the aggregate of ferromagnetic particles should have a width $\Delta H \cong 10^2 - 10^3$ Oe.

Actually, broad lines of this type were observed in epr spectra of samples containing ferromagnetic particles [5,6]. However, under some conditions we can also expect the appearance of much narrower ferromagnetic resonance lines in small ferromagnetic particles. We have already indicated above that in particles for which $K\bar{v} < kT$, the spontaneous magnetization vector $\overline{\mathbf{M}} = \mathbf{I}_0\bar{v}$ should fluctuate in direction, and this circumstance is equivalent to Brownian rotation of the particle. Investigating the mechanism of fluctuations of this type, Neel has shown [7] that an individual ferromagnetic particle should experience elastic fluctuational deformations. The resultant fluctuations in the magnetoelastic energy should lead to precession oscillations of its spontaneous magnetization vector **M**. Although Neel's calculation is based on macroscopic concepts, it nevertheless makes it possible to estimate the angular frequency Ω of these oscillations:

$$\Omega = \frac{3\lambda\gamma}{I_0}\sqrt{\frac{2GkT}{\pi\bar{v}}}. \qquad (6)$$

Here λ is the magnetostriction constant, G the shear modulus of the particle material, and γ the coefficient of spectroscopic splitting of the electron spin.

Let $\Delta\omega = \gamma\Delta H$ be the frequency corresponding to the line width ΔH (5). According to the general theory of magnetoresonance phenomena, the fluctuation oscillations of the vector **M** should narrow down the resonance line in the case when

$$\Omega > \Delta\omega. \qquad (7)$$

At room temperature this condition can be realized, in accordance with (5) and (6), only for particles for which

$$\bar{v} < 9G\lambda^2\pi kT / 2K^2. \qquad (8)$$

Substituting in (8) the usual values for λ, G, and K, namely $\lambda = 10^{-5} - 10^{-6}$, $G = 10^{12}$ dyne/cm^2, and $K = 10^4 - 10^5$ erg/cm^3, we see that the narrowing down of the ferromagnetic resonance lines can take place only for particles whose average volume is

$$\bar{v} < 10^{-18} - 10^{-20}\ \text{cm}^3,$$

that is, the mean diameter is $d < 10^{-6} - 10^{-7}$ cm.

We thus arrive at the important conclusion that ferromagnetic particles with a total of $n < 1000$ spins can serve under certain circumstances as a source of very narrow ferromagnetic resonance lines. There are grounds for assuming that such ferromagnetic resonance lines can be mistaken for epr lines of individual unpaired spins, free radicals, etc.

Incidentally, it must be borne in mind that, unlike epr lines, the width ΔH of "narrow" ferromagnetic resonance lines should increase with decreasing temperature.

We now turn to the question of the effect produced on the epr spectrum of a liquid dielectric of ferromagnetic particles suspended in it. Inasmuch as rotational Brownian motion of the particles takes place in the liquid, macroparamagnetic properties should now be displayed by all particles; this should be manifest in the ferromagnetic resonance intensity. However, Brownian rotational motion of particles does not affect the width of the ferromagnetic resonance lines, since the average angular frequency of the Brownian rotation Ω' is much smaller than $\Delta\omega$. In fact (for spherical particles),

$$\Omega' = \sqrt{2kT/\pi\eta d^3} = \sqrt{kT/3\eta\bar{v}}, \tag{9}$$

where η is the viscosity of the liquid. For $\eta = 2 \times 10^{-2}$ (water) and $\bar{v} \cong 10^{-20}$ cm^3, we get $\Omega'/\Delta\omega = 10^{-6}$, that is, $\Omega' \ll \Delta\omega$.

The general conclusions obtained here call of course, for further development of the theory and for a thorough experimental verification.

In conclusion I am sincerely grateful to G. V. Skrotskiĭ and R. M. Rozman for a critical discussion of the foregoing considerations.

[1] W. Clemm, Magnetochemistry (Russ. Transl.) IIL, 1939.

[2] P. Selwood, Magnetochemistry (Russ. Transl.) IIL, 1960.

[3] S. A. Al'tshuler and B. M. Kozyrev, Electronnyi paramagnitnyĭ rezonans (Electron Paramagnetic Resonance), Fizmatgiz, 1961.

[4] C. P. Bean and J. D. Livingston, J. Appl. Phys. Suppl. 30, 120 (1963).

[5] Ya. G. Dorfman, DAN SSSR 142, 815 (1962), Soviet Phys. Doklady 7, 121 (1962).

[6] Ya. G. Dorfman, Zhurn. Strukt. Khimii (J. Struct. Chem.) 4, 624 (1963).

[7] L. Neel, Ann. Geophysique 6, 99 (1949).

Translated by J. G. Adashko
92