The Magnetization of Ferromagnetic Colloids

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The magnetization curves of colloidal magnetite (Fe_3O_4) and colloidal siderac ($\gamma-Fe_2O_3$) have been determined by a null method for fields from 0 to 400 gauss. The measured curves have been found to agree with a theoretical curve based on the following assumptions: (1) Each colloid particle is a permanent magnet. This assumption is in accord with a prediction of the theory of ferromagnetism that small ferromagnetic particles be single magnetic domains. (2) There exists a distribution in the size of the particle moments similar to the weight distributions which have been found for other colloids. (3) The particles behave as the molecules of a classical paramagnetic gas. On this basis the average particle moment is found to be $5.2(10)^{-16}$ for the magnetite sol and $7.4(10)^{-16}$ for the siderac sol. Several other quantities related to the colloids are briefly discussed.

IN a recent note[1] the writer described the preparation of a colloidal magnetite suitable for studying magnetic structures by the magnetic powder method.[2] For various reasons it appeared interesting to investigate the magnetization curve of such a colloid, particularly since the magnetic properties of ferromagnetic colloids for the most part have escaped the attention of other workers. Knowledge of the magnetization curve should be useful for estimating the intensity of the stray fields responsible for the powder patterns. As a first step towards such an estimation the present study has been devoted to determining and analyzing the magnetization curves of two different ferromagnetic colloids which have been used in powder pattern investigations.

A number of years ago Frenkel and Dorfman[3] predicted from energy considerations that sufficiently small ferromagnetic particles (diameter 100 mμ or smaller) should be single ferromagnetic domains. An attempt by Montgomery[4] to verify this prediction for nickel colloids was unsuccessful, probably because the nickel oxidized before measurements could be made. As pointed out by Montgomery,[3] if the colloid particles be small permanent magnets, they should behave as the molecules of a classical paramagnetic gas obeying the Langevin equation

$$I = I_s\,(\coth a - 1/a) = I_s L(a) \qquad (1)$$

where $a = \mu H/kT$. Since the magnetic moment per particle μ would have a value much larger than that of a single atom, saturation effects in weak fields ($a \geq 1$) should be easily observed. It will be shown that the magnetization curves for two different iron oxide colloids are actually similar to the Langevin curve, but that before a quantitative agreement can be made, it is necessary to modify the Langevin curve by assuming a distribution in the size of the particle moments. In addition, values of I_s must be taken smaller than those expected from the amount of iron present as determined by chemical analysis.

METHOD OF MEASUREMENT AND SPECIMENS

Measurements were made by a null method. In a circuit containing a sensitive ballistic galvanometer the additional flux linkage produced by the sample was balanced by setting a calibrated mutual inductance. The arrangement used, shown by diagram in Fig. 1, was designed by Professor F. Bitter for the measurement of susceptibilities of the order of 10^{-3}. M_1 and M_2 were two mutual inductances made as nearly identical as possible and connected in opposition. The secondary coils, 5 cm long, contained 10,000 turns of fine wire. The primary coils, 25 cm long, had a mean diameter of 2.3 cm and produced a nearly uniform magnetizing field $H = 41.9i$ over the length of the inner coil. M_3 was a Leeds &

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[1] W. C. Elmore, Phys. Rev. **54**, 309 (1938).

[2] F. Bitter, *Introduction to Ferromagnetism* (McGraw-Hill Book Co., 1937), pp. 55–66.

[3] J. Frenkel and J. Dorfman, Nature **126**, 274 (1930). See also C. G. Montgomery, Phys. Rev. **38**, 1782 (1931).

[4] C. G. Montgomery, Phys. Rev. **39**, 163 (1932).

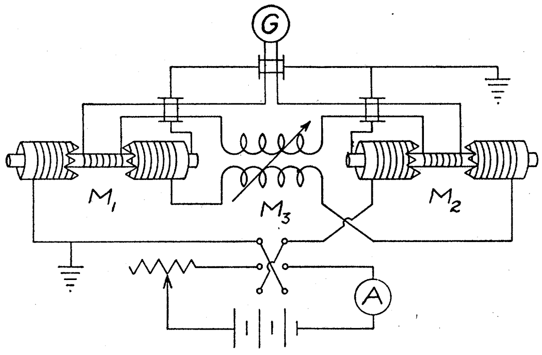

FIG. 1. Diagram illustrating the method used for measurements.

Northrup variable mutual inductance having a range +0.06 to −0.06 millihenry and safely passing 10 amperes. To prevent galvanometer drift, all secondary leads were shielded. The shields, the brass tubes on which M_1 and M_2 were wound, and one point of the primary circuit were all grounded.

For measurement, the colloid sample was drawn into the inner tube of M_1 which was mounted with its axis vertical. The zero balance was easily checked after allowing the sample to drain out. For large currents M_3 could be set for no galvanometer deflection directly to $(10)^{-7}$ henry by momentarily closing the primary circuit several times. For smaller currents, where the heating of the magnetizing coils was negligible and where the galvanometer deflections were smaller, a number of deflections each side of the balance point were taken by reversing the primary current. The balance point was then determined graphically to almost the same precision as for the larger currents. The measurements made by this method were good to a few percent.

By a simple analysis, the equations for the susceptibility k and the intensity of magnetization I of the colloid are the following:

$$k=\frac{(\Delta M)i(10)^8}{4\pi ANH}=54.3(\Delta M), \qquad (2)$$

$$I=\frac{(\Delta M)i(10)^8}{4\pi AN}=0.227(\Delta M)i, \qquad (3)$$

where ΔM = change in setting of M_3 (in henries) required for balance when the sample is introduced; i = magnetizing current in amperes; A = cross-sectional area of sample = 0.350 cm^2; N = number of turns in secondary of M_1 = 10,000; H = magnetizing field = $41.9i$ gauss. The greatest current used was about 10 amperes; the values for ΔM ranged between the limits $2.7(10)^{-6}$ and $17(10)^{-6}$ henry.

Two different specimens were investigated: one, the magnetite sol prepared as already described;[1] the other, a sample of colloidal gamma-ferric oxide (siderac) prepared several years ago by means of a colloid mill by Sharp and Dohme of Philadelphia, Pennsylvania. The sample measured had remained undisturbed in a corked bottle for more than a year so that all coarse particles had settled out. Chemical analyses for total iron content[5] indicated that the two specimens contained iron equivalent to a

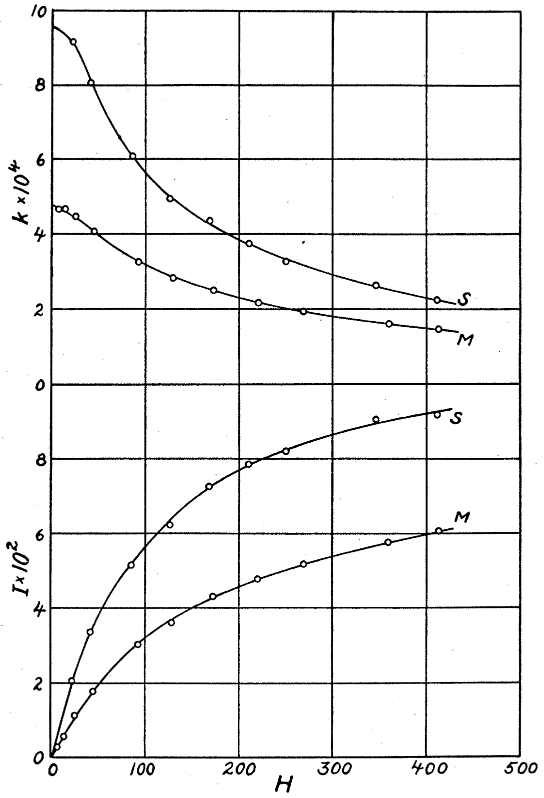

FIG. 2. Curves showing the dependence on field strength of the susceptibility and the intensity of magnetization for the magnetite colloid (curves M) and the siderac colloid (curves S).

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[5] Kindly made by A. Klemka, Department of Chemistry, Massachusetts Institute of Technology.

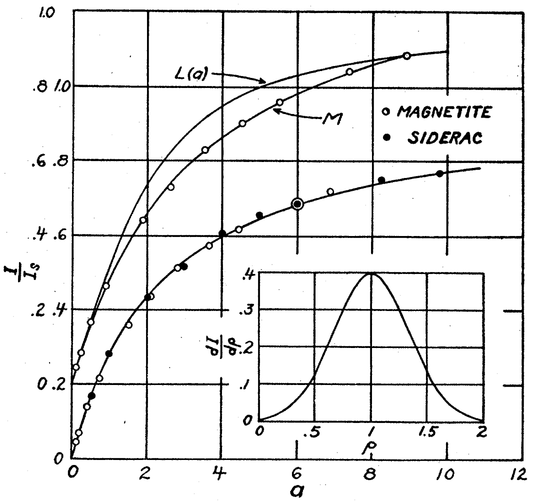

FIG. 3. Upper curves illustrate the poor agreement between the Langevin curve and the experimental curve for magnetite. Lower curve is the modified Langevin curve obtained by assuming the particle moment distribution shown in the insert. The experimental points for both colloids fit the modified curve within the experimental error.

concentration 0.00206 g/cm^3 of Fe_3O_4 and 0.00420 g/cm^3 of Fe_2O_3, respectively. All measurements were made at a room temperature of 27°C.

RESULTS AND DISCUSSION

The experimental curves for k and I *versus* H are shown in Fig. 2 for both the magnetite sol (curves *M*) and the siderac sol (curves *S*). In Fig. 3 (upper curves) the magnetization curve *M* has been fitted to the Langevin curve so that the two curves coincide at their extremities and have the same slope at the origin. This procedure amounts to choosing values for I_s and μ in Eq. (1). The agreement is by no means satisfactory and is no better for the siderac sol.

To improve matters, several possibilities have been considered. In particular it is suggested that a distribution in the size of the particle moments may be responsible for the discrepancy between the experimental and Langevin curve. The measurements of particle size distributions in colloids have been few in number and of fairly recent date. Using an ultracentrifuge, Nichols, Kraemer and Bailey[6] determined the (optical) weight distribution as a function of particle diameter r for certain iron oxide colloids. They found fairly broad distributions approximately Gaussian in shape. If the magnetic moment per particle is assumed proportional to the volume of the particle ($\mu = \text{const.}\ r^3$) then distribution in magnetic moments should be similar to the weight distributions. The expression

$$dI/d\rho = (B/\pi^{\frac{1}{2}}) \exp\left[-B^2(1-\rho)^2\right], \qquad (4)$$

where $\rho = r/r_0$ and B is a constant, is a Gaussian distribution about the particle diameter r_0. When $B \doteq 3/\sqrt{2}$ it is very similar to the weight distributions which have been found for other colloids. A smaller value of B leading to a broader distribution is not possible since an appreciable area under the distribution curve would then lie to the left of the origin $\rho = 0$. Hence if the distribution (4) with $B \geq 3/\sqrt{2}$ does not happen to lead to an agreement between experiment and theory it will be necessary to assume a non-Gaussian distribution or to invoke a different mechanism to account for the shape of the magnetization curves. Fortunately this has not been found necessary.

The magnetization curve appropriate to the distribution (4) with $B = 3/\sqrt{2}$ can be calculated from the integral

$$I = I_s \frac{3}{(2\pi)^{\frac{1}{2}}} \int_0^\infty \exp\left[-9(1-\rho)^2/2\right] L(a_0\rho^3)\, d\rho, \qquad (5)$$

where $a_0 = \mu_0 H/kT$ and μ_0 is the moment of a particle having the diameter r_0. The integral (5) has been evaluated numerically for a number of values of a_0, giving the lower curve in Fig. 3. The curve has been plotted by taking $a = 4a_0/3$ so that its initial slope is the same as that of $L(a)$. The experimental points for both colloids have been fitted to this curve by the method previously used for the Langevin curve, giving an agreement which is now within the experimental error for both colloids. In Table I the constants needed to produce this fit have been collected, together with other related quantities. As an insert in Fig. 3 is shown the distribution (4) with $B = 3/\sqrt{2}$.

In the table μ_0 is not the most frequently occurring particle moment but the moment which corresponds to the peak in the distribution (4). The saturation moment per unit volume I_s is

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[6] J. B. Nichols, E. O. Kraemer and E. D. Bailey, J. Phys. Chem. 36, 326 (1932).

that occurring in Eq. (5). Its values are to be compared with those of I_s' which have been computed from the chemically determined colloid concentrations and the specific intensities of magnetization for the two oxides as reported in the literature.[7] The estimated diameter r_0 of a particle of moment μ_0 has been calculated from the expression

$$\mu_0=(\pi/6)(I_s/I_s')I_0r_0^3, \tag{6}$$

where I_0 is the bulk saturation intensity of magnetization for magnetite or siderac,[8] and where the particle has been assumed spherical.

Several possible explanations can be offered to account for the difference between the values of I_s and I_s'. The most likely explanation is that a considerable portion of the iron determined by chemical analysis (good to four percent) was not present as magnetite or siderac but as some other nonferromagnetic oxide of iron. For instance, it was observed that prolonged shaking in a test tube oxidized the reddish-black magnetite sol into one which was deep red in color and nonferromagnetic.

TABLE I. *Constants chosen for best fit of experimental points to Eq. (5).*

	μ_0	I_s	I_s'	I_s/I_s'	r_0
magnetite	$5.2(10)^{-16}$	0.084	0.192	0.44	17 mμ
siderac	$7.4(10)^{-16}$	0.120	0.319	0.38	21 mμ

Other factors which could reduce the observed values of I_s have to do with the nature of the colloid particles. Only if the particles be single crystals free from serious imperfections does it seem likely that they would be single magnetic domains, i.e., domains in which all the elementary magnets are in a parallel alignment throughout the particle. In addition the values of I_s may be reduced by the relatively large number of atoms present on the surface of the particles. For instance, if a particle contains $(10)^5$ atoms, about 13 percent of the atoms will not be completely surrounded by neighbors. Although it is not possible at present to estimate the importance of the various factors which have just been discussed, it is a fair conclusion that small ferromagnetic particles are not demagnetized in the macroscopic sense of the word, in agreement with the prediction of Frenkel and Dorfman.[3] Certainly no macroscopic magnets of spherical shape exhibit a remanence comparable with that observed for the colloid particles.

The author is greatly indebted to Professor F. Bitter, Department of Metallurgy, for the loan of the apparatus with which measurements were made, and for interesting discussions about the ferromagnetism of small particles.

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[7] P. Weiss and R. Forrer, Ann. de physique **12**, 279 (1929).

[8] In obtaining I_0 the densities of the two oxides have been taken as 5.2 and 5.1 g/cm^3, respectively.