Interpretation of Ferromagnetic Colloid Patterns on Ferromagnetic Crystal Surfaces

W. C. ELMORE

Department of Physics, Swarthmore College, Swarthmore, Pennsylvania

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It is shown that the bodily motion of particles rather than a magneto-optic effect is chiefly responsible for field-induced changes in ferromagnetic colloid patterns on ferromagnetic crystal surfaces. A simple relation between colloid concentration and magnetic field intensity near the crystal surface is deduced from the Boltzmann distribution law. Several implications of this relation are discussed, including the role played by magnetic interaction of the particles. The formation of elongated chains of particles in a colloid placed in a magnetic field is shown to be unlikely provided that the particles are sufficiently small in size.

IN a recent note[1] L. W. McKeehan has suggested that a magneto-optic effect, similar to the action of a magnetic field on the optical transparency of a magnetite suspension, may play a role in determining the apparent distribution of ferromagnetic colloid in patterns on polished silicon-iron crystals.[2] According to Heaps[3] suspended particles of magnetite form elongated groups under the action of an applied magnetic field, making the suspension more transparent parallel to the field and less transparent perpendicular to it. McKeehan points out that this phenomenon rather than the bodily motion of colloid particles can be used to explain the shifting of pattern lines observed when an applied normal field is reversed. Before citing experimental evidence which does not support this view, it is pertinent to mention some qualitative results of the magneto-optic experiment performed with ferromagnetic colloids which have been used for magnetic structure studies.

The ferromagnetic colloids show changes in transparency parallel and perpendicular to an applied magnetic field opposite to those shown by a coarse ferromagnetic suspension. Majorana[4] has reported that certain nonferromagnetic colloids of $Fe(OH)_3$ show a similar anomalous effect in a very intense field. In the present case changes in transparency tend to saturate at a few hundred oersteds, and they are greater with siderac-dextrin colloid prepared by a colloid mill[5] than with magnetite-soap colloid prepared by chemical means.[6] The anomalous effect lacks a simple explanation, but its existence somewhat modifies the suggested magneto-optical explanation of field-induced pattern changes.

Several observations have been made which support the view that the pattern changes produced by reversing an applied normal field are caused by the bodily motion of colloid particles rather than by the magneto-optic effect. Under high magnification (1500×) with vertical illumination it is possible to identify individual particles in a pattern by virtue of the Tyndall effect. The particles appear to be buzzing around in Brownian motion and a swarm of them can be seen to move from one region to another when the stray field is modified by an applied field. Their motion can be seen even more clearly with dark-field illumination as furnished by the Leitz Ultrapak, for with this illuminator the particle swarms appear light against a dark background. Even at low magnification the field-induced motion of unresolved colloid swarms can often be inferred from the visible motion of a few relatively large particles which may be present. It is evident that the magneto-optic effect can at most play a minor role in governing the appearance of patterns.

The problem of the distribution of colloid particles on the surface of a ferromagnetic crystal can be approached from the point of view of statistical mechanics. The following analysis applies when mutual action between particles

[1] L. W. McKeehan, Phys. Rev. **57**, 1177 (1940).

[2] L. W. McKeehan and W. C. Elmore, Phys. Rev. **46**, 226 (1934).

[3] C. W. Heaps, Phys. Rev. **57**, 528 (1940); see, also, W. C. Elmore, Phys. Rev. **57**, 842 (1940).

[4] Q. Majorana, Acc. Lincei, Rendiconti [6a] **29**, 11 (1939).

[5] W. C. Elmore, Phys. Rev. **51**, 982 (1937).

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

can be neglected, i.e., when the particles behave as an ideal gas. The effect of magnetic interaction will be mentioned later.

Let $\mathbf{H}(x, y, z)$ represent the magnetic field above the plane surface of a ferromagnetic crystal, the normal to the surface coinciding with the z axis. It is most convenient to consider the crystal as being a thin slab or disk having a demagnetization factor 4π so that an applied normal field $\mathbf{H}_0$ of moderate intensity will not appreciably magnetize the crystal, but will simply add vectorially to its stray field. Since the latter field is negligible except near the surface of the crystal, $\mathbf{H}(x, y, z) = \mathbf{H}_0$ for values of $z \gg d$, where d is the separation of pattern lines. Now consider the crystal to be covered by a ferromagnetic colloid containing, at a distance from its surface, n_0 particles per unit volume, each particle having a permanent magnetic moment μ. According to the Boltzmann distribution law, the number of particles in a volume dV lying with their axes in the solid angle $d\omega$ is given by

$$d^2N = Ce^{\mu H \cos \theta / kT} d\omega dV$$

$$= 2\pi Ce^{a \cos \theta} \sin \theta d\theta dV, \quad (1)$$

where $a = a(x, y, z) = \mu H/kT$, θ is the angle between μ and $\mathbf{H}$, C is a constant and kT has its usual meaning. At equilibrium the concentration of particles n, at a point where the intensity of the field is H, is given by

$$n = \frac{dN}{dV} = 2\pi C \int_0^\pi e^{a \cos \theta} \sin \theta d\theta = 4\pi C \sinh a/a$$

$$= n_0(a_0/\sinh a_0)(\sinh a/a), \quad (2)$$

where the constant C has been evaluated from the condition that when $H = H_0(a = a_0)$, $n = n_0$.

To illustrate the application of Eq. (2) let us consider a crystal whose stray field is derivable from the potential $V = H_s(d/\pi)e^{(-\pi z)/d} \cos (\pi y/d)$. The intensity of this field is independent of y and has the value H_s at the crystal surface. Let us suppose, for example, that $H_s = 500$ oersteds. If we take $\mu = 5 \times 10^{-16}$ as a reasonable value for the magnetic moment of the particles,[7] it follows that $a = 6.1$ at the crystal surface, and from Eq. (2), $n \doteq 30n_0$. If now there be superposed a

uniform normal field of 80 oersteds directed away from the surface, the field intensity at lines on the surface given by $y = 0$, $2d$, $4d$, $\cdots$ will be 580, whereas at lines given by $y = d$, $3d$, $5d$, $\cdots$ it will be only 520. The corresponding values of a will be, respectively, 7.1 and 5.1, and those of n, $80n_0$ and $15n_0$. The position of these maximum and minimum concentrations of colloid will be interchanged if the field direction is reversed. In the preceding calculation $a_0 \doteq 1$ so that in Eq. (2) $a_0/\sinh a_0 \doteq 1$. With more intense fields this approximation cannot be made, for instance, if $H_0 = 250$, the two sets of lines will have the concentrations $150n_0$ and n_0, respectively. This suggests that it may be possible in certain cases to estimate the intensity of the stray field by finding the applied normal field which just removes the colloid from one set of pattern lines. The maximum normal stray field will then have twice this value. Now the no-field distribution of colloid produced by the simple periodic field under discussion shows no pattern lines. Either a slight magnetic particle interaction,[8] or the magneto-optic effect could result in the appearance of a double set of lines. The analysis predicts, in agreement with observation, that the total amount of colloid drawn to the surface is greater when there is an applied field present. On removing the field more than an equilibrium amount of colloid is gathered near the surface so that the no-field pattern is considerably more dense than it otherwise would be.

It is possible to take into account magnetic interaction of colloid particles by assuming that each particle is subject to, in addition to the external field, (1) the Lorentz field $(4\pi/3)I$, and (2) a demagnetizing field due to volume and surface distributions of magnetic poles in the colloid. By means of Langevin's equation, $I = n\mu(\coth a - 1/a)$, which has been shown to hold approximately for ferromagnetic colloids;[7] and Eq. (2), which relates colloid concentration to field intensity, the increase in concentration resulting from mutual action of the particles can be estimated. The increase is found to be small and ordinarily can be neglected provided that

[7] W. C. Elmore, Phys. Rev. **54**, 1092 (1938).

[8] In reference 5 where particle interaction is mentioned a mistake in sign resulted in an incorrect drawing (Fig. 3) showing the distribution of particle dipoles above the surface of a crystal. The layer of dipoles should be inverted and shifted sideways a distance d.

sufficiently fine colloids are used. A rough estimate of particle diameter required for the formation of magnetically linked chains of particles can be made by equating kT to the maximum mutual magnetic energy of a pair of particles in contact. If it is assumed that the particles are spheres of diameter D, and that each particle is a single ferromagnetic domain having an intensity of magnetization I, then $kT = \mu^2/D^3 = (\pi^2/36)I^2D^3$. By taking $I=450$ for magnetite and $kT=4.1 \times 10^{-14}$ it follows that for chain formation $D \geq 40$ mμ, to be compared with an estimated mean particle diameter of 17 mμ for colloidal magnetite.[7] Now the calculated value (40 mμ) is undoubtedly low on several counts: (1) the intensity of magnetization is considerably less than 450;[7] (2) the protective colloid (soap) increases the distance of closest approach between two particles; and (3) repulsive forces of electrical origin exist among the particles. Hence we may conclude that chain formation should be expected with suspensions, but not with colloids whose particle size is, for instance, 100 mμ or less.

A Method for Obtaining Powders of Uniform Sodium Chloride Crystals in Various Size Ranges, and the Effect of Size upon the Intensity of X-Ray Reflection

Fitz-Hugh Marshall
University of Chicago, Chicago, Illinois
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I. A technique is presented for precipitating powders of sodium chloride crystals, uniform in size and cubical in shape, in various size ranges from 1 to 70 microns, above which the range could be extended by screening. The crystals are prepared by precipitation with absolute ethyl alcohol from a saturated solution of sodium chloride in water, but varying excess quantities of water are added to either of the solutions before combining them. Control of size range, and of crystal uniformity within a size range, is accomplished by careful attention to certain primary variables in the precipitation process, each of which produces marked changes in the character of the powder obtained. These are discussed, and a simplified procedure is presented for producing any desired size. II. This technique was developed to make possible a study of the variation of intensity of x-ray lines reflected from such size-graded powders. The 200-reflection of Cu $K\alpha$ radiation has been investigated, and a curve is shown for the variation of intensity with crystal size. The intensity decreases slightly with increase of crystal size, according to a curve which indicates that the crystals are imperfect but are more perfect than large single crystals.

I. A Method for Obtaining Powders of Uniform Sodium Chloride Crystals in Various Size Ranges

Introduction

FINE crystalline powders, rather than single large crystals, have been used in many quantitative measurements on the intensity of x-ray reflections. Comparison of results with theory has invariably involved the assumption that the individual crystals are so small, 10^{-5} cm or less, as to offer negligible x-ray absorption. Most investigators have been greatly concerned with the degree of subdivision of their powders, and a few have ground powders successively finer until intensity determinations leveled off to constant values;[1] but on the whole, there has been no attempt at a systematic study of reflection from powders of crystals larger than allowed by simple theory. It seemed desirable, therefore, to develop a reproducible technique for making uniform crystals of various sizes and to investigate their x-ray reflections. Sodium chloride was selected for study.

Sodium chloride powders have generally been prepared either by prolonged grinding or by precipitation. Grinding produces such an irregular debris of all sizes and shapes of particles

[1] R. J. Havighurst, Phys. Rev. **28**, 882 (1926).