

Magnetic Properties of Mixed Ferrites

II. Superparamagnetism and Exchange Anisotropy in a Cobalt-Zinc Ferrite

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Abstract. The form of the magnetic isothermals of a bulk specimen of the ferrite $\text{CoO}_{0.13}\text{ZnO}_{0.75}\text{Fe}_2\text{O}_3$ between 77°K and room temperature indicates the presence of strongly magnetic particles of maximum diameter about 40 \AA in a superparamagnetic state dispersed in a non-magnetic matrix. Cooling in an applied field down to 4.2°K produces a displaced hysteresis loop characteristic of unidirectional exchange anisotropy. The coercivity at 4.2°K after cooling in zero field is about 5000 Oe .

§ 1. INTRODUCTION

WHEN a magnetic material owes its bulk magnetic properties to the presence of a dispersion of non-interacting magnetic particles in an unmagnetized matrix, the magnetic behaviour will under some conditions depend in a marked way on the size of the particles. For instance, if the particles are single domains and if they are small enough their magnetic energy ($-MH$) in practical field strengths H may be no greater than their thermal energy kT . There will be a tendency with decreasing particle size towards a state where the particle magnetization has random direction although the particles themselves are in an intrinsic sense spontaneously magnetized to saturation. This is the state first discussed by Stoner (1936) and Néel (1949) and called superparamagnetism by Bean (1955).

The observed specific magnetization σ of a superparamagnetic assembly is given as a fraction of the intrinsic magnetization σ_1 by

$$\frac{\sigma}{\sigma_1} = \coth \alpha - \frac{1}{\alpha} \quad (1)$$

where $\alpha = MH/kT$. M is the magnetic moment of the particle under consideration and is given by $m\sigma_1$, where m is its mass.

Thus, for a superparamagnetic material which is far enough below its intrinsic Curie point for σ_1 to be effectively independent of temperature, measured magnetizations should follow a universal variation with H/T for different fields and temperatures, in contrast to the usual behaviour of ferromagnetics. Where σ_1 varies with temperature, σ/σ_1 should follow a similar universal variation with H/T .

The initial susceptibility is given by

$$\left(\frac{d\sigma}{dH} \right)_{H \rightarrow 0} = \frac{\sigma_1^2 m}{3kT}. \quad (2)$$

This leads to estimates of the particle mass m when σ_1 is known. σ_1 may be measured as the value of σ extrapolated to where $1/H = 0$ from measurements in strong fields.

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Also, in the region where saturation is being approached,

$$\left(\frac{d\sigma}{d(1/H)}\right)_{1/H \rightarrow 0} = -\frac{kT}{m} \tag{3}$$

from which the particle mass can also be estimated. Usually the treatment is somewhat complicated by the presence of a range of particle masses.

This paper deals with the properties of the cobalt-zinc mixed ferrite $\text{CoO}_{0.18}\text{ZnO}_{0.75}\text{Fe}_2\text{O}_3$, which appears to fit into the above framework.

§ 2. EXPERIMENTAL TECHNIQUES AND SPECIMEN PREPARATION

The apparatus used was similar to that described in (Booth and Crangle 1962, to be referred to as I) except for certain modifications which enabled measurements to be performed down to the temperature of liquid helium (see Scott and Crangle 1961). The preparation of the material and its subsequent chemical and x-ray analysis are also described in I.

§ 3. RESULTS AND DISCUSSION

3.1. Properties above 77° K

A set of magnetic isothermals measured at temperatures between 77° K and room temperature is shown in figure 1. Over the whole of this temperature range the remanent magnetization was insignificantly small, rising to a value of 1.5 e.m.u. g⁻¹ on cooling to 77° K.

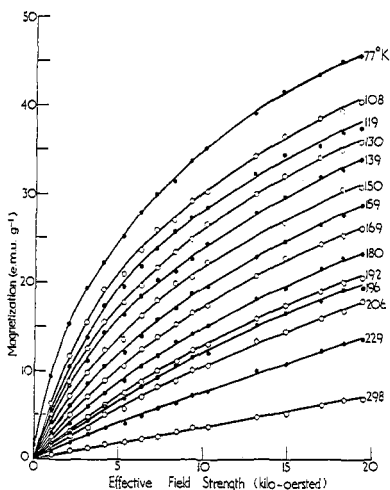


Figure 1. Magnetic isothermals of $\text{CoO}_{0.18}\text{ZnO}_{0.75}\text{Fe}_2\text{O}_3$ from 77° K to room temperature. Full and open circles are used to distinguish the alternate curves.

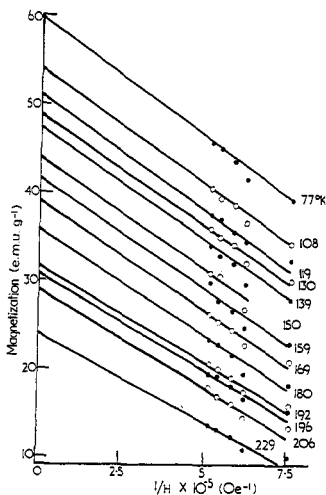


Figure 2. Magnetization σ plotted against $1/H$ for various temperatures.

The magnetizations measured in the highest field strengths (up to 20 kilo-oersteds) varied almost linearly with $1/H$, allowing estimates to be made of the saturation magnetization σ_1 (figure 2). In figure 3 a universal plot of σ/σ_1 as a function of H/T is given for a number of widely different temperatures. The degree to which overlap occurs in this diagram seems to confirm that the material does behave superparamagnetically.

As is usual in superparamagnetic systems, the points in figure 3 cannot be fitted exactly to the simple Langevin function (1) for a single value of α , presumably because a range of different particle masses is present. However, the quality of the approximate fit is shown in figure 3, where the curved line represents a Langevin function. Calculation of particle mass from the measured initial susceptibilities at various temperatures by means of equation (2) gives values m_1 lying between 0.8×10^{-19} and 1.4×10^{-19} g.

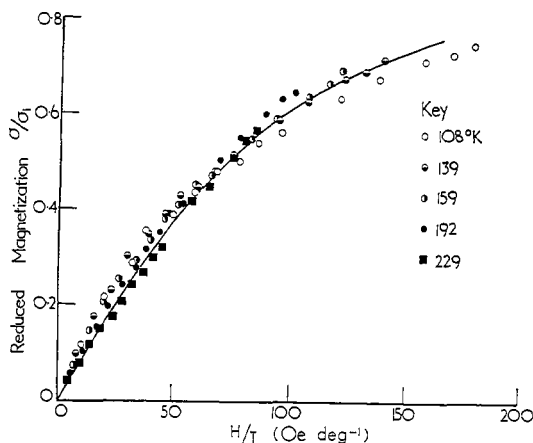


Figure 3. Reduced magnetization σ/σ_1 plotted against H/T from data at five temperatures. The continuous line is calculated from the Langevin function and normalized to the experimental points at $H/T = 125$.

Masses m_2 obtained through equation (3) from the rate of approach to saturation at each temperature lie between 0.4×10^{-19} and 1.6×10^{-19} g. The initial susceptibility is sensitive to the larger particles present, while the approach to saturation depends more on the smaller particles. Treatments in which a particular numerical distribution of particle sizes was assumed, for example by Becker (1957) and by Henning and Vogt (1957), suggest that the mean value of m_1 will be an underestimate of the maximum mass of particle present, but will be correct within a factor of two, and likewise that m_2 will be an overestimate of the true mass of the smallest magnetic particle.

If the mean maximum mass of the magnetic particles is about 2×10^{-19} g and we assume a density of 5, the maximum diameter of equivalent spherical particles is 40 Å.

In figure 4 the approximate values of σ_1 are plotted against temperature. The intrinsic Curie point is probably of the order of 270°K , and the value of σ_1 at 0°K is about 61 e.m.u. g^{-1} .

3.2. Properties below 77°K

At low temperatures the material becomes ferromagnetic, with finite remanence and a hysteresis loop, but even at 4.2°K saturation is not achieved in an applied field of 20 kilo-oersteds. The coercivity at this temperature is about 5000 oersteds. Such a high value of coercivity does not appear to have been reported previously in bulk specimens of an oxide having the spinel structure, although Berkowitz and Schuele (1959) obtained values of nearly 7000 oersteds at 77°K in micropowders of cobalt ferrite, the particle diameter being about 300 Å. Berkowitz and Schuele suggested that their powder contained a large concentration of single domain particles, and that magnetocrystalline anisotropy is the dominant factor contributing to the large coercivity.

Cooling the specimen in an applied magnetic field of +18.4 kilo-oersteds from 77°K to 4.2°K causes the hysteresis loop to become displaced, indicative of the presence

of exchange anisotropy (figure 5). The coercivities become -5700 and $+3800$ oersteds on the two sides of the loop, while the remanence values are $+22.0$ and -17.0 e.m.u. g^{-1} . Reheating to about $20^\circ K$ and cooling again to $4.2^\circ K$ in zero applied field makes the remanence almost symmetrical at ± 19 e.m.u. g^{-1} , but the coercivity remains slightly asymmetrical at -5000 and $+4700$ oersteds.

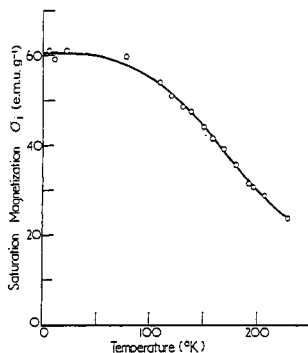


Figure 4 Variation of saturation magnetization σ_1 with temperature for $CoO_{0.18}ZnO_{0.75}Fe_2O_3$.

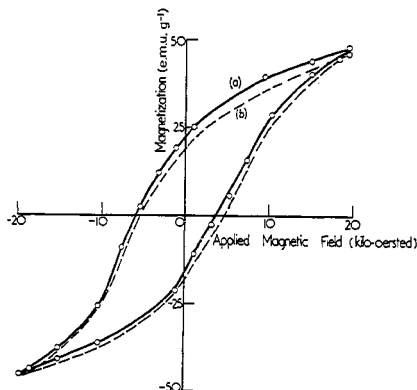


Figure 5. Hysteresis loops measured at $4.2^\circ K$: (a) after cooling in a field of $+18.4$ kilo-oersteds, and (b) after warming to $20^\circ K$ and recooling to $4.2^\circ K$ in zero applied field.

The occurrence of the displaced hysteresis loop after cooling in a field suggests that the specimen consists of a mixture of ferromagnetic (or, more exactly, ferrimagnetic) and antiferromagnetic components; that exchange coupling exists over the boundaries between them, of the kind first discussed by Meikeljohn and Bean (1956, 1957) with reference to mixtures of ferromagnetic Co and antiferromagnetic CoO; and that the direction of the magnetization of the ferromagnetic part at the time of cooling through the Néel temperature of the antiferromagnetic part tends to become locked unidirectionally. That the displacement of the hysteresis loop is relatively small in this case suggests that by no means all of the ferromagnetic component is affected in this way.

The antiferromagnetic part of the specimen would seem to be of normal type, where antiferromagnetic BB interactions dominate. Pure zinc ferrite is like this and has a Néel point of $9^\circ K$ (Hastings and Corliss 1956). The ferromagnetic part is probably made up of residual microscopic regions of inverse structure, where the divalent cations are predominantly situated on octahedral (or B) crystallographic sites.

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