observed decay time of the radiation being less than 1 μsec is consistent with the recombination lifetime expected from the measured efficiency.

Electroluminescence has been reported in CdS also by Boer and Kummel[3] and by Diemer.[4] In both cases activated crystals (photosensitive) were used. Boer and Kummel operated their crystals at liquid air temperature and obtained green and red emission. Diemer observed yellow spots at the tip of the anode and orange-red flames in the crystal. These workers ascribe the electroluminescence they observe to the action of a high electric field on electrons and do not consider hole injection. Although our crystals are considerably different from theirs, the $I-V$ characteristics are nearly identical. We emphasize the abrupt increase in current coincident with the appearance of the yellow patches at the anode, at which point we believe holes are injected into the crystal.

V. ACKNOWLEDGMENT

This study was initiated under the direction of Dr. A. Rose. The author is indebted to him for many stimulating discussions and for his continued interest.

PHYSICAL REVIEW VOLUME 105, NUMBER 3 FEBRUARY 1, 1957

New Magnetic Anisotropy

W. H. MEIKLEJOHN AND C. P. BEAN
General Electric Research Laboratory, Schenectady, New York
(Received October 15, 1956)

A new type of magnetic anisotropy has been discovered which is best described as an exchange anisotropy. This anisotropy is the result of an interaction between an antiferromagnetic material and a ferromagnetic material. The material that exhibits this exchange anisotropy is a compact of fine particles of cobalt with a cobaltous oxide shell. The effect occurs only below the Néel temperature of the antiferromagnetic material, which is essentially room temperature for the cobaltous oxide. An exchange torque is inferred to exist between the metal and oxide which has a maximum value at 77°K of $\sim$2 dyne-cm/cm^2 of interface.

INTRODUCTION

A NEW discovery has been made in the field of magnetic materials that manifests itself in the form of a displaced hysteresis loop[1] as shown in Curve 1, Fig. 1. In addition, although from the same basic phenomena, the magnetic material has only one stable orientation in a magnetic field. In particular, it can be turned through 180° and it will still return to its original orientation.

The material that exhibits this property is a compact of fine particles of cobalt (100–1000 A) that have a cobaltous oxide coating. The compact exhibits the normal behavior of a symmetrical hystersis loop (Curve 2, Fig. 1) when cooled to 77°K in the absence of a field, but when cooled to 77°K in a strong magnetic field it exhibits the displaced hysteresis loop (Curve 1, Fig. 1).

Before this discovery, the known methods of increasing the coercive force of a material involved the strain, crystalline anisotropy, and shape anisotropy. We now have an additional mechanism involving an interaction between an antiferromagnetic material and a ferromagnetic material. Since the origin of this effect is postulated as being an interaction between the spins of the cobalt atoms in the metal and the cobalt ions in the antiferromagnetic cobaltous oxide, it might properly be termed an exchange anisotropy. It is shown by experiment that this coupling results, for a specific case, in an exchange anisotropy constant of the same order of magnitude as the crystalline anisotropy of cobalt (5×10^6 ergs/cc).

[1] W. H. Meiklejohn and C. P. Bean, Phys. Rev. **102**, 5, 1413 (1956).

TORQUE AND ENERGY FUNCTION

The new properties of this material are best described by comparison with well-known materials. Let us consider a small spherical single-domain particle of cobalt *without* an oxide coating as our classical material.

If the particle of pure cobalt is cooled to liquid nitrogen temperature in a strong magnetic field, say 20 000 oersteds, it will exhibit a normal symmetrical hysteresis loop of the type shown in Fig. 2(a). A torque curve taken on this material would be a sin 2θ function as shown in Fig. 2(b). Hence,

$$T=-\partial E/\partial\theta=-K_1\sin2\theta,$$

$$E=\int K_1\sin2\theta d\theta=K_1\sin^2\theta+K_0.$$

Therefore the energy function would be as shown in Fig. 2(c), where it is apparent that energy minima occur at $\theta=0$ and $\theta=180°$. That is, both directions along the c axis of the cobalt particle would be in stable equilibrium in an infinite field at $\theta=0$ and $\theta=180°$.

Now let us consider the oxide-coated particle of cobalt that has a displaced loop of the type shown in

Fig. 3(a). The torque curve obtained in a random compact of such particles is shown in Fig. 3(b), i.e.,

$$T=-\partial E/\partial\theta=-K_u \sin\theta;$$

hence,

$$E=\int K \sin\theta d\theta=-K_u \cos\theta+K_0.$$

Therefore the energy function is as shown in Fig. 3(c) where it is apparent that an energy minimum occurs only at $\theta=0$. This oxide-coated particle is in stable equilibrium in the field only at $\theta=0$. The particle will always return to its original position no matter how far it is displaced. The sole limitation in the field is that it be less than the threshold fields in the antiferromagnet.[2] A compact of the oxide-coated material was exposed to a field of 70 000 oersteds and still exhibited a displaced hysteresis loop.

Let us now consider the hysteresis loop that would be obtained if the energy function were exactly given by

$$E=-K \cos\theta$$

and the hysteresis loss in the material is extremely small, that is, a soft magnetic material. In a later section it is shown that the hysteresis loop would be as shown in Fig. 4. We now have a magnet that cannot be demagnetized by any magnetic field, since it would end up, with the field removed, at point a or b on the load line that is characteristic of the dimensions of the magnet.

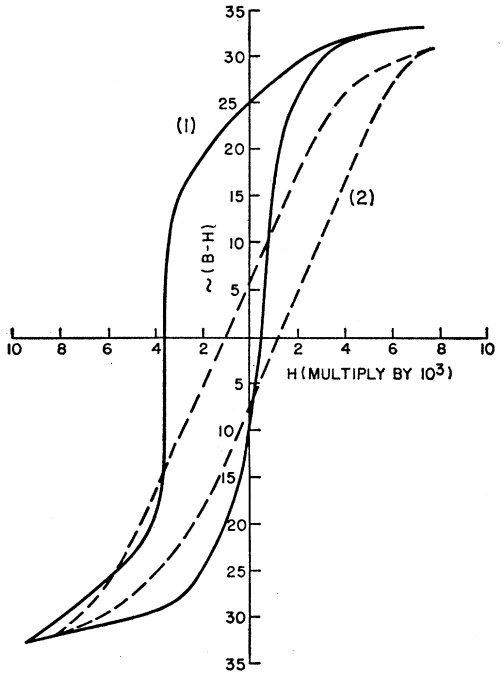

FIG. 1. Hysteresis loops at 77°K of oxide-coated cobalt particles. Solid line curve results from cooling the material in a 10 000 oersted field. The dashed line curve shows the loop when cooled in zero field.

[2] L. Néel, *Le Dixième Conseil de Physique Solvay* (R. Stoops, Brussels, 1955), p. 251.

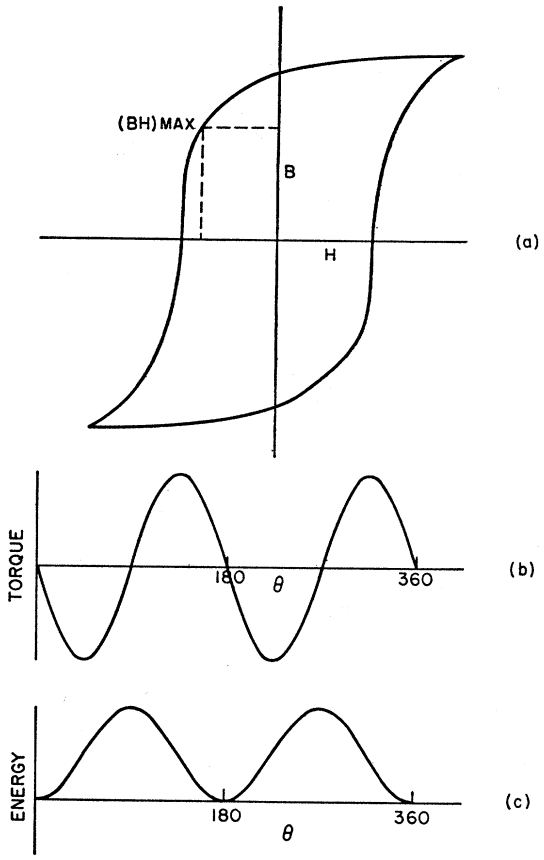

FIG. 2. Hysteresis loop (a), torque curve (b), and energy curve (c), for conventional cobalt particles. (No oxide coating.)

Of course loop displacement of a "hard" magnetic material is also very beneficial. Displacement of the loop increases the energy product and therefore makes a better permanent magnet material. Oxide-coated cobalt particles have been compacted to give an energy product of 4×10^6 gauss-oersteds at $B=2000$ gauss and $H=2000$ oe, in a material containing only 25% cobalt by weight.

MANUFACTURE

The material is made by the electrodeposition of cobalt into a mercury cathode. The 600-ml beaker contains 80 cc of mercury and 40 grams of cobaltous ammonium sulfate dissolved in 400 ml of distilled water (0.35 Molar). The bath is heated to a temperature of 40–50°C. Plating is carried out for 1 hour at 3 amp (5.6 amp/cm²).

The mercury containing the cobalt is then removed and heat treated in an air oven at 140°C for 10 minutes. The material is placed in a "Mercury Oxifier" for about 8 hours and the oxide-coated cobalt particles float to the surface of the mercury. These particles are removed

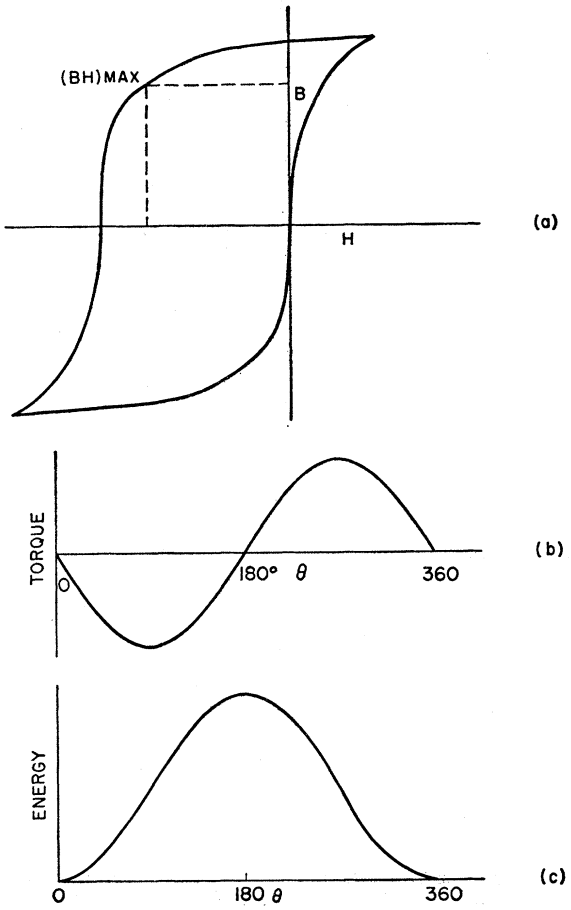

FIG. 3. Hysteresis loop (a), torque curve (b), and energy curve (c), for oxide-coated cobalt particles below Néel temperature of oxide.

by using a magnet. The mercury carried over in the process can be removed by vacuum distillation.

THEORY OF THE DISPLACED HYSTERESIS LOOP

If we consider a spherical single-domain particle with uniaxial anisotropy of $K_1 \sin^2\theta$, where θ is the angle between the easy direction of magnetization and the direction of magnetization, and further assume that the easy direction is the field direction, then the free energy, at absolute zero, of the particle in a field H oppositely directed to that of magnetization, is written

$$F=HI_s \cos\theta+K_1 \sin^2\theta.$$

Taking the derivative of this free energy with respect to θ and examining the nature of the maximum and minima, one obtains the familiar result that the hysteresis loop is square and the intrinsic coercive force has a value

$$_iH_c=2K_1/I_s.$$

If one introduces *ad hoc* a unidirectional anisotropy of the form

$$-K_u \cos\theta,$$

the expression for the free energy becomes modified to read

$$F=HI_s \cos\theta-K_u \cos\theta+K_1 \sin^2\theta;$$

thus the solution is identical with the previous case with the substitution of an effective field

$$H'=H-K_u/I_s,$$

which gives the hysteresis loop displaced on the H scale by K_u/I_s.

The explanation of the loop displacement is seen to be equivalent to explanation of the unidirectional anisotropy.

NECESSARY CONDITIONS FOR LOOP DISPLACEMENT

The occurrence of the displaced hysteresis loop is definitely brought about by the existence of an oxide film on the particles of cobalt. This has been established by two experiments.

The particles of cobalt, prepared by the electrodeposition of cobalt into a mercury cathode, are free of any appreciable oxide and are wet by the mercury. The properties of the cobalt particles were measured while in the mercury and they showed a normal hysteresis loop. When the mercury containing the particles was placed in a mercury oxifier and an oxide coating was formed on the particles, the magnetic measurements showed a displaced hysteresis loop.

The second experiment that established the oxide coating as a necessary condition involved the removal

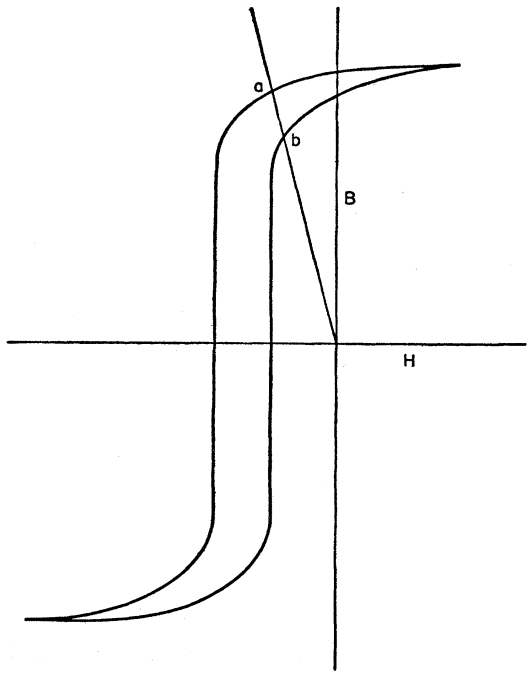

FIG. 4. Possible hysteresis loop for a normally soft magnetic material with exchange anisotropy. Points *a* and *b* are the intersections of the hysteresis loop with a load line.

TABLE I. Effect of hydrogen reduction and re-oxidation of the oxide-coated cobalt.

	A Starting material	*B* H_2 for 2 hr at 200°C	*C* O_2 for 1 hr at 20°	*D* O_2 for 4 hr at 20°	*E* O_2 for 14 hr at 100°C
${}_rH_c$ (oe)	750	825	1325	1450	750
${}_fH_c$ (oe)	−1725	−850	−1350	−1450	−1725
${}_rB_r$ (arbitrary units)	−2.6	−9.8	−9.0	−9.3	−5.0
${}_fB_r$ (arbitrary units)	8.7	10.2	9.7	9.8	8.1
B_s (arbitrary units)	10	20	18	18	11

of the oxide coating by hydrogen reduction. The magnetic hysteresis loop again became normal. Upon subsequent oxidation the hysteresis loop became displaced.

The starting material had the properties shown in Table I, Column *A*, where ${}_fH_c$ and ${}_rH_c$ represent the intrinsic coercive forces in the forward and reverse directions, ${}_fB_r$ and ${}_rB_r$ represent air-gap remanence in the forward and reverse directions in arbitrary units, as shown in Fig. 5, and B_s the saturation flux density. Annealing this material in dry hydrogen for two hours at 200°C gave the results shown in Column *B*. Passing oxygen at room temperature over the sample for one hour gave the results shown in Column *C*. Three more hours of oxidation gave the results shown in Column *D*. Passing dry oxygen for 14 hours at 100°C gave the results shown in Column *E*.

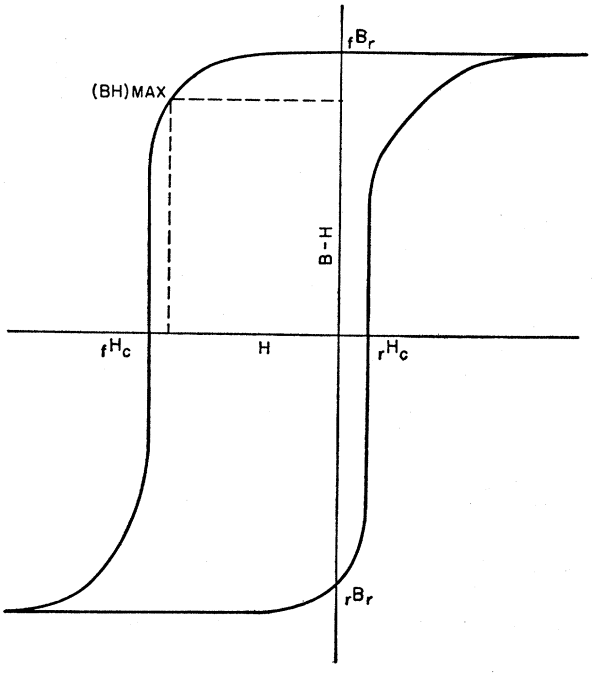

FIG. 5. Schematic hysteresis loop of the new material to illustrate the definitions of the forward and reverse remanences and coercive forces.

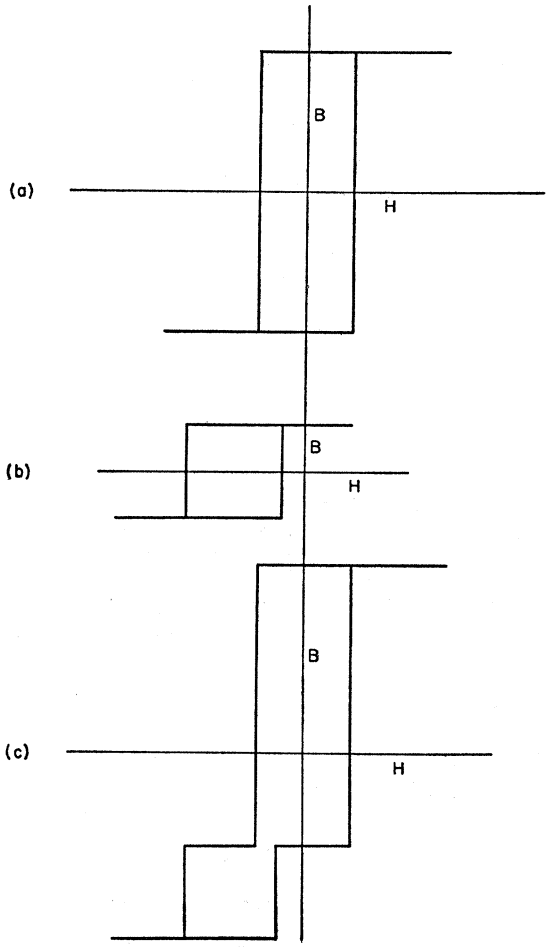

FIG. 6. Schematic hysteresis loops proposed to show how a material may show asymmetry in *B*, but not in *H*. (a) Nonshifted material. (b) Shifted loop material. (c) Mixture of (a) and (b) material.

Several things may be noted from the data in Table I. From the reduction in B_s in Columns *A* and *E* it is apparent that approximately half of the cobalt in the initial and final states is nonmagnetic and presumably in the form of cobalt oxide. While the coercive force can be made quite symmetric by hydrogen reduction, the remanent magnetizations do not become so and thus constitute a more sensitive test for asymmetry than the coercive force measurements. An idealized explanation of this is shown in Fig. 6. A large amount of material which has a symmetric loop, assumed straight-sided, is represented by *A* and a smaller amount of material *B* with an asymmetric loop, also assumed straight-sided, is represented by curve *B*. If these hysteresis loops are added, assuming no interactions, curve *C* results. Curve *C* exhibits an asymmetric remanence while the coercive force is symmetric.

The oxide coating on the cobalt has been established by electron diffraction measurements to be CoO. The

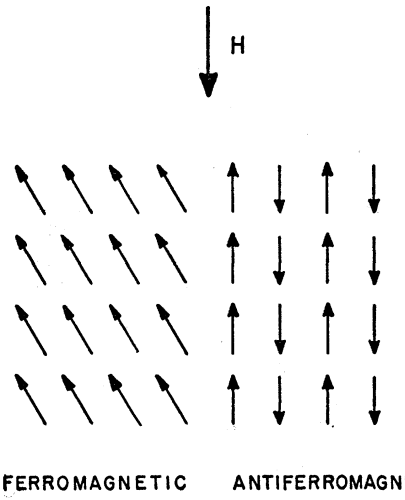

FIG. 7. A schematic picture of the ferromagnet-antiferromagnet interface with a small applied field.

electron diffraction data taken by Walter[3] are shown in Table II. This result is in agreement with cobalt and oxygen phase diagram of Seybolt and Mathewson,[4] shows that CoO is in equilibrium with Co at room temperature.

Experiments designed to evaluate the influence of the thickness of the oxide film on the displacement of the hysteresis loop have yielded ambiguous information, probably due to a variation in particle size that results in complete oxidation of some very small particles and makes measurements of the degree of oxidation by saturation measurements unreliable. In addition the particle size of the unoxidized cobalt is important. This has been partly established by oxidizing particles grown to 1000 A particle size. These particles show the loop displacement but to a much lesser degree.

There is some indication that a certain oxide thickness is necessary to produce the shift in the hysteresis loop. Oxide-coated cobalt has been made that initially did not show a shifted loop, but at a much later date (1 month) did show a loop shift. This may have been due to continual oxidation of the powder, resulting in a sufficient oxide thickness to produce a loop shift. However, another interpretation would be that the particles were not completely covered with oxide (some mercury still wetting patches of the particle) and subsequent oxidation of these patches produced the effect.

TABLE II. Comparison of tabulated x-ray spacings for CoO and those observed on oxidized cobalt particles.

CoO A	2.45	2.12	1.50	1.28	1.23	1.06	0.98	0.95	0.87	0.82
Observed A	2.46	2.13	1.50	1.29	1.24	1.07	0.98	0.95	0.87	···

[3] N. M. Walter (private communication).
[4] A. U. Seybolt and C. H. Mathewson, Trans. Am. Inst. Mining Met. Engrs. 3 (1934).

MICROSCOPIC MECHANISM OF LOOP DISPLACEMENT

Since the usual sources of anisotropy—crystal, shape, and magnetostriction—are symmetric with respect to inversion of the magnetization, it is clear, from experiments reported later in the paper, that the antiferromagnetic nature of the cobaltous oxide surface layer is responsible for this effect. Below the Néel temperature, the spins of the cobalt ions in the cobaltous oxide will tend to align themselves in antiferromagnetic alignment. The neutron diffraction studies of Shull, Strauser, and Wollan[5] show that the spins lie along [100] directions and like spins are on (111) planes. Recent work by Roth[6] of this Laboratory confirms the latter observation but places the spin directions in the (111) planes.

Paine[7] suggested the kernel of the following explanation. If we consider a condition of oxidation in which a

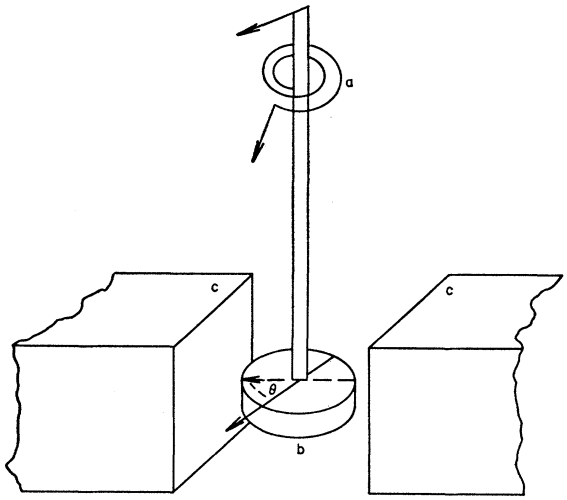

FIG. 8. Schematic diagram of the torque tester. Its main component is a spring (a) which measures the torque on a sample (b) in the field of an electromagnet (c).

surface of the cobalt metal is coherent with (111) plane of the cobaltous oxide (Fig. 7), then if there is exchange coupling across this interface there will be, at the time of cooling through the Néel temperature, a selection among the various equivalent spin directions in the oxide due to this interaction. If the sample is now cooled to a low temperature at which the anisotropy of the cobaltous oxide is large, then, by the same interaction, the moments of the cobalt will tend to stay aligned in one direction along the axis of spin alignment in the oxide. If the volume and anisotropy constant of the oxide are large in comparison to the torque exerted across the interface, this restoring force will exist for all fields. A unidirectional anisotropy will result in the

[5] Shull, Strauser, and Wollan, Phys. Rev. 83, 333 (1951).
[6] W. L. Roth (private communication).
[7] T. O. Paine (private communication).

compact for material cooled through the Néel temperature in the presence of an orienting field. If the material is cooled in the absence of a field, the unidirectional exchange anisotropy exists within each particle but it is unobservable in the compact because of the random directions of anisotropy axes. Appendix I contains a more detailed account of a theory of this effect.

TORQUE MEASUREMENTS

The most useful data for explaining the nature of the loop displacement have been obtained from torque measurements. These data yield information about the anisotropy constant and the form of the energy function.

A torque magnetometer was designed to measure the anisotropy in the material induced by cooling in a magnetic field. Figure 8 shows the method of measurement. When the sample, in the form of a disk, is placed in the field, with the field making an angle θ with the

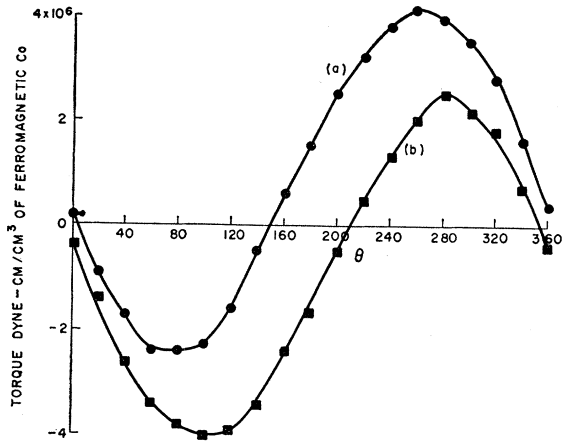

FIG. 9. Torque curves on oxide-coated cobalt particles cooled in a field to 77°K, where θ is the angle between the cooling-field axis and the direction of the measuring field as shown in Fig. 8. Curves (a) and (b) are for rotations of decreasing and increasing θ, respectively.

direction of original field present during cooling, it experiences a torque tending to return it to the original field direction. This torque is balanced by a torque from a phosphor bronze spring attached between the sample axis and turning handle. The deflection of a scale attached to this spring is then a measure of the torque.

By appropriate choice of springs, torque sensitivities from 178 dyne-cm per degree deflection to 1790 dyne-cm per degree are obtained.

A compact of cobalt particles with cobaltous oxide coatings gave no measurable change of torque with angle on being cooled in a demagnetized state, showing the absence of any crystal orientation in the compact. In contrast, a typical curve of torque *versus* angle for material cooled in a field is shown in Fig. 9. This disk, $\frac{1}{4}$ in. in diameter by $\frac{1}{4}$ in. high containing 38 mg of ferromagnetic cobalt, was cooled to liquid nitrogen temperature in a field of 20 000 oe and the torque was

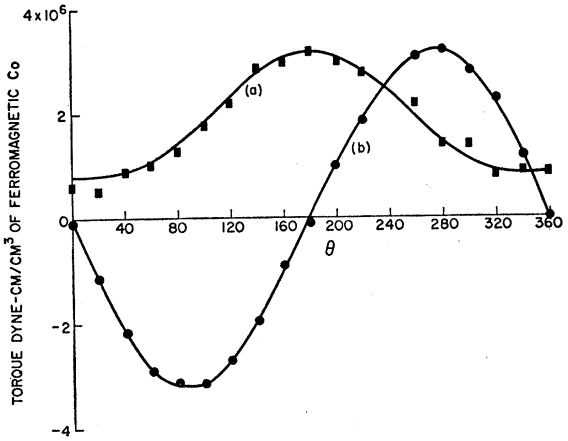

FIG. 10. Torque curves on oxide-coated cobalt particles. (a) Difference in torque curves of Fig. 9 for both directions of rotation of the sample in the magnetic field; (b) the average torque curve of Fig. 9 for both directions of rotation.

measured at this temperature in a field of 7500 oe. The measurements are made after cycling both clockwise and counterclockwise directions. In addition to showing the uniaxial characteristic of the anisotropy, the curves indicate a considerable rotational hysteresis. In Fig. 10, (curve b), the average of the torque values for both directions of rotation is plotted as a function of angle, representing the "true" torque curve. In addition, the difference in torque values (curve a) represents the rotation hysteresis. The empirical equations for the curves plotted in Fig. 10 are: average torque $T=3.2_6\times10^6\sin\theta+0.1\times10^6\sin2\theta$ dyne-cm per cc of ferromagnetic cobalt, and rotational torque $R=0.8\times10^6+2.4\times10^6\sin^3(\theta/2)$. The rotational hysteresis is given by

$$W_{\text{rot}}=\frac{1}{2}\int_0^{2\pi}Rd\theta=5.7\times10^6 \text{ (ergs/cycle) per cc of ferromagnetic cobalt.}$$

To deal with the rotational hysteresis, the values are plotted in Fig. 11 as a function of inverse field strength. In contrast with normal ferromagnetic materials in which this quantity approaches zero as the field becomes infinite or saturation becomes complete, the

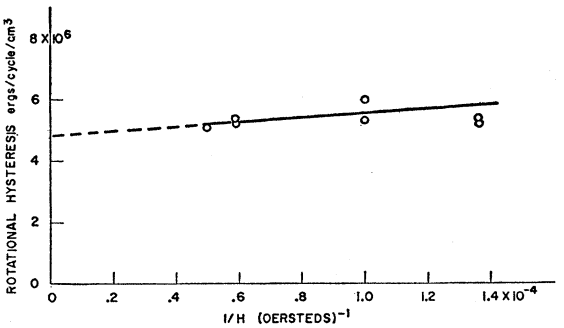

FIG. 11. Values of the rotational hysteresis extrapolated to infinite measuring field.

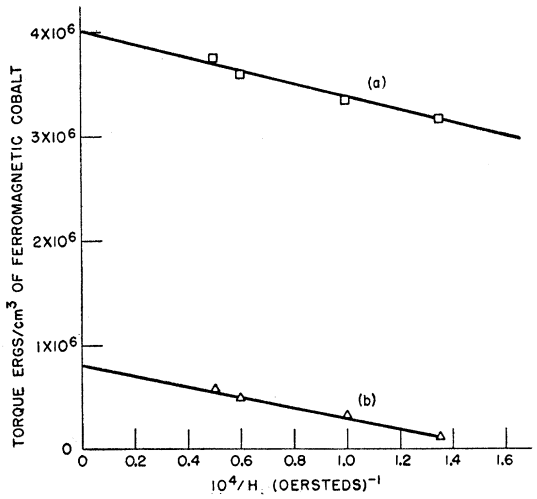

FIG. 12. Maximum torque values for oxide-coated particles extrapolated to infinite measuring fields. (a) Maximum torque values for $\sin\theta$ component; (b) maximum torque values for $\sin 2\theta$ component.

rotational hysteresis varies only by 12% with an almost threefold variation in field. This singular behavior can be qualitatively understood from the model proposed for this interaction.

In the case of thin oxide-coated cobalt particles, there is discontinuous reorientation of the spins in the oxide layer, that occurs because of its interaction with the magnetization of the cobalt. Hysteresis results from discontinuous change of magnetization. In the case of normal ferromagnetic materials exposed to magnetic fields above the anisotropy field, the magnetization has no discontinuities in its motion about the field axis and consequently the rotational hysteresis is zero. The antiferromagnetic cobalt oxide feels only the interaction with the magnetization of the cobalt and not the external field directly so that when sufficient field to substantially rotate the magnetization of the cobalt has been applied and if the oxide layer is thin enough, there will be a discontinuous reorientation of the spins in the oxide layer. This behavior can be used as an evidence for the existence of the interaction.

The values of the torque maxima are plotted in Fig. 12 (curve a) as a function of $1/H$, with the magnitude of the $\sin 2\theta$ component of the anisotropy (curve b). Table III contains the analysis of the average torque curves. All terms beyond $\sin 2\theta$ in the Fourier expansion do not have statistically significant amplitudes.

TABLE III. Analysis of torque curves of particles cooled in 20 000 oersted field to 77°K.

H oersteds	K_1 ergs/cm³ of Co	K_2 ergs/cm³ of Co
7500	3.16×10^6	0.16×10^6
10 000	3.33×10^6	0.32×10^6
17 000	3.60×10^6	0.52×10^6
20 000	3.74×10^6	0.56×10^6

UNIAXIAL ANISOTROPY AND LOOP SHIFT *VS* I/I_s

The postulated mechanism suggests that the uniaxial anisotropy and loop shift would rise more rapidly than the relative magnetization at the time of quenching, since the last few degrees of rotation of the magnetization would favor no anisotropy axis in the cobaltous oxide that were not favored at the lower magnetization.

Data at 77°K on uniaxial anisotropy as a function of degree of saturation of magnetization while cooling through the Néel temperature are shown in Fig. 13, while the data on the loop shift as a function of the degree of saturation are shown in Fig. 14. The shape of the curves for the experimental data taken at −196°C (curve a) and −68°C (curve b) show that the loop shift does increase rapidly at low fields and saturate at high fields as expected.

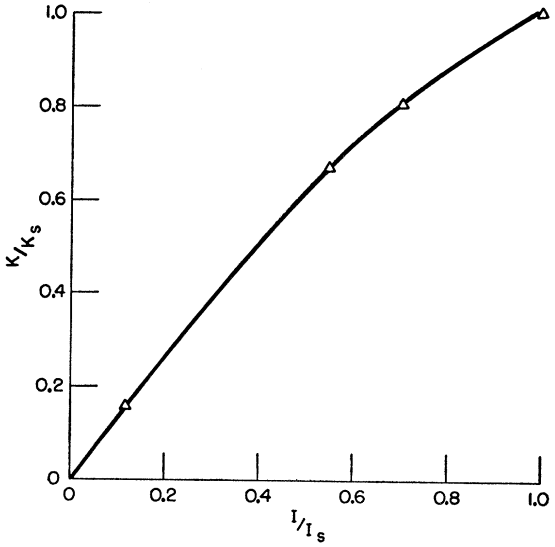

FIG. 13. Dependence of the reduced sin θ anisotropy on the reduced magnetization. The magnetization is that caused by the magnetic field in which the particles are cooled to 77°K.

LOOP SHIFT *VS* TEMPERATURE

The results of two experiments designed to determine the correlation of the loop shift with the Néel temperature of CoO are shown in Figs. 15 and 16. According to measurements by Fine,[8] and by Street and Lewis,[9] CoO is paramagnetic above approximately 300°K. If antiferromagnetic cobaltous oxide causes the loop shift, we should find that above 300°K the material acts like a normal magnetic material and exhibits no loop shift, while below 300°K the loop shift should exist and increase in magnitude as the temperature is lowered.

The experimental results shown in Fig. 15 were obtained by cooling the material in a 10 000-oersted field from room temperature to the temperature given by the abscissa and by then removing the field and

[8] M. E. Fine, Revs. Modern Phys. **25**, 158 (1953).
[9] R. Street and B. Lewis, Nature **168**, 1036 (1951).

cooling the material to liquid nitrogen temperature in order to have a constant reference temperature (liquid nitrogen temperature) in each case. The loop shift is greatest when the sample is cooled to a low temperature in the magnetic field and drops to zero near the Néel temperature (270°K) of CoO.

Since the residual field of the specimen was present after removal of the external magnetic field, the material was not cooled from the temperature of the abscissa, in Fig. 15, to liquid nitrogen temperature in a zero field as was desired. To eliminate this difficulty the following experiment was performed in collaboration with I. S. Jacobs. These data are shown in Fig. 16. A sample of this type of material was demagnetized and cooled in the absence of an external field to a temperature T_0 then placed in a field of 10 000 oersteds and cooled to −196°C where ${}_fH_c$ (curve d) and ${}_rH_c$ (curve a) were measured. From these data we obtained the shift in the hysteresis loop (curve b) and the half-width

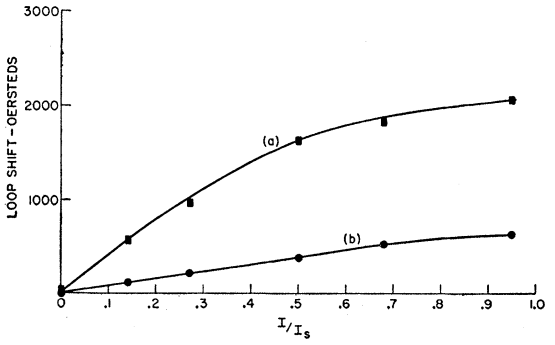

FIG. 14. Loop shift as a function of reduced magnetization. (a) Data at 77°K; (b) data at 205°K. The magnetization is caused by the magnetic field in which the particles are cooled through the Néel temperature.

of the loop (curve c) defined by $({}_fH_c-{}_rH_c)/2$. The effect begins between 0°C and −20°C showing a rough equivalence to the Néel temperature of cobaltous oxide (−2°C). That the initiation of this effect should occur somewhat below the Néel temperature is not unexpected since the critical factor is the anisotropy energy of the spin system in the cobaltous oxide. This energy would be expected to rise monotonically with decreasing temperature and to exceed the critical value for a given particle, above which the direction of magnetization of the cobalt ions in the cobaltous oxide will be held in a direction close to the field cooling direction, only somewhat below the Néel temperature. Of interest, also, is the fact that the half-width of the hysteresis loop increases when the uniaxial character appears. This may be explained by the concomitant appearance of a $\sin^2\theta$ term in the anisotropy which, as in the well-known theory of the coercive force of single-domain particles, will lead to an increased coercive force. This term can come from thin cobaltous oxide shells in which the spin

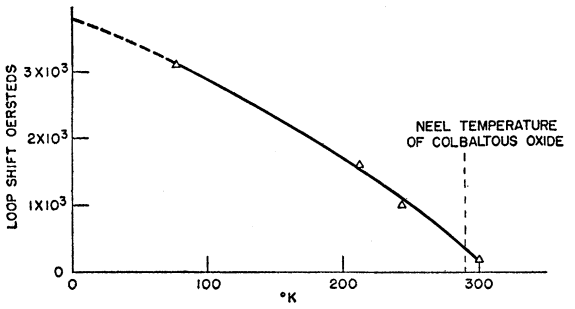

FIG. 15. Loop shift as a function of temperature to which the specimen is cooled in a 10 000-oersted field.

system in the cobaltous oxide will rotate with that of the cobalt, as discussed in Appendix I.

Both sets of data yield the result that above the Néel temperature, where the CoO is paramagnetic, the material behaves in a normal manner, while below the Néel temperature, where the CoO is antiferromagnetic, a loop shift occurs.

INFLUENCE OF PACKING

There is no influence due to density of packing on the coercive force of particles that derive their coercive force from exchange anisotropy. This behavior is to be contrasted with that for particles that derive their coercive force from shape anisotropy,[10–12] where theory

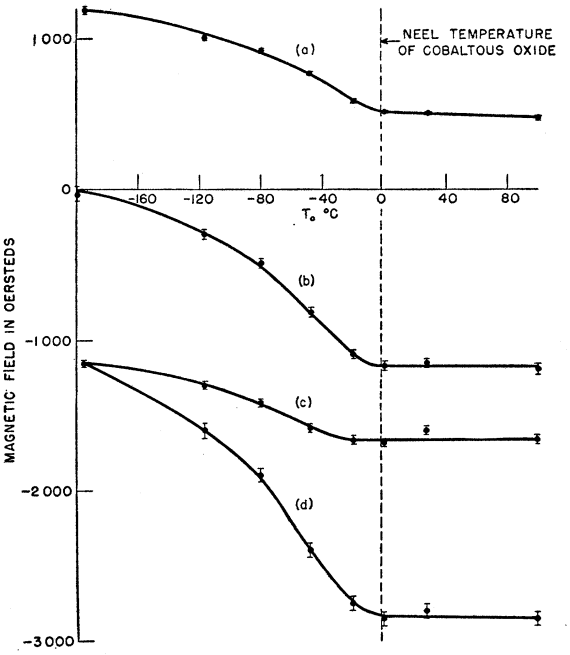

FIG. 16. Data showing correlation of loop shift with Néel temperature of cobaltous oxide. T_0 is the temperature to which the material was cooled in a demagnetized state prior to further cooling in a 10 000 oersted field at 77°K. Curves (a), (b), (c), and (d) show ${}_rH_c$, $({}_fH_c+{}_rH_c)/2$, $({}_fH_c-{}_rH_c)/2$, and ${}_fH_c$, respectively, as functions of T_0. All measurements are made at 77°K.

[10] L. Néel, Compt. rend. **224**, 1550 (1947).
[11] E. Kondorskii, Compt. rend. **80**, 197 (1951).
[12] E. P. Wohlfarth, Proc. Roy. Soc. (London) **A232**, 208 (1955).

and experiment show that the coercive force is given approximately by

$$_iH_c(f)=(1-f)_iH_c,$$

where f= the volume fraction of ferromagnetic material, $_iH_c$= intrinsic coercive force at infinite dilution, and $_iH_c(f)$= intrinsic coercive force for packing fraction f. Particles with exchange anisotropy were tested with packing factors that varied from 0.01 to 0.25 and there was no influence on the measured coercive force.

ACKNOWLEDGMENTS

We wish to acknowledge the help and suggestions of I. S. Jacobs, T. O. Paine, and W. L. Roth, which have greatly contributed to this work.

APPENDIX I

The simplest model of this phenomenon is to consider a hypothetical system consisting of a ferromagnetic particle with uniaxial anisotropy possessing a coherent layer of an antiferromagnetic substance, again with a uniaxial anisotropy axis coincident with that of the ferromagnetic material. It must be assumed that some interfaces have unequal numbers of antiparallel moments in the plane of the antiferromagnetic lattice adjacent to the interface or more particularly the interfacial plane could be a plane of parallel moments in the antiferromagnet. This proviso is essential to develop the torque between the two lattices which is essential to the effect. A further simplifying assumption is that the exchange torque is much weaker across the interface than in either the ferromagnetic particle or the antiferromagnetic shell, and further that both the particle and the shell are so small that they can be treated as single-domain particles with all their interaction absorbed across the interface. Designating the angles of the magnetization in the ferromagnet and antiferromagnet by θ and θ_1, respectively, we denote the respective anisotropies by $K_1\sin^2\theta$ and $K_0\sin^2\theta_1$. The exchange interaction across the interface shall be a restoring of the form $-E\sin(\theta-\theta_1)$, where E has the units of dyne cm/cm^2 of interface. In addition we shall require the angle, ϕ, which the external field, H, makes with the anisotropy axis and further shall designate the radius of the metallic cobalt particle by r, and the radius of the entire particle including the oxide shell by r_0. We may identify five torques in this system, and in each case we shall refer the torques to a unit volume of cobalt since this is the easiest experimental measurement. The five torques are:

T_1, the torque exerted by the external field on the magnetization of the cobalt,

$$T_1=HI_s\sin(\phi-\theta);$$

T_2, the ferromagnetic anisotropy torque exerted by the lattice upon the magnetization of the cobalt,

$$T_2=-K_1\sin2\theta;$$

T_3, the exchange torque exerted by the cobaltous oxide on the magnetization of the cobalt,

$T_3=-E\sin(\theta-\theta_1)$ multiplied by the interfacial area divided by the volume of cobalt

$$=-(3E/r)\sin(\theta-\theta_1);$$

T_4, the antiferromagnetic anisotropy torque exerted by the cobaltous oxide lattice on the spins of the cobaltous oxide,

$T_4=-K_0\sin2\theta_1$ multiplied by the volume of cobaltous oxide divided by the volume of cobalt

$$=-K_0\sin2\theta_1(r_0^3/r^3-1);$$

T_5, the torque exerted by the particles on the torque magnetometer.

Since in equilibrium the torque on the magnetization of the cobalt must be zero,

$$T_1+T_2+T_3=0. \tag{1'}$$

Equally, the torque on the spins of the antiferromagnet must be zero, giving

$$-T_3+T_4=0. \tag{2'}$$

The torque on the torque magnetometer, T_5, is the sum of the torques on the lattices

$$T_5=-T_2-T_4,$$

which in combination with the earlier equations yields for the external torque,

$$T_5=T_1. \tag{3'}$$

Equations (1') and (2') must be solved for θ and θ_1 and the results compared by Eq. (3') to the experimental data to infer the unknown constants E and K_0. The simplest case is to assume the anisotropy is very large for an infinitesimal θ_1, i.e., $\theta_1=0$. In this case, Eq. (1') gives

$$T_1=K_1\sin2\theta+(3E/r)\sin\theta,$$

and for very high fields θ is almost precisely equal to ϕ and so the measured torque becomes independent of field and

$$T_1=K_1\sin2\phi+(3E/r)\sin\phi. \tag{4'}$$

In the sample we measured, the anisotropy axes of the various cobalt particles were at random with respect to any direction in the compact so that the first term averages to zero while the coefficient of the second would be modified by a factor of 0.5 to 1.0 depending on the number of easy directions in the oxide. Thus, Eq. (4') when averaged gives the torque curve experimentally observed. The observed torque constant is 4×10^6 dyne-cm/cm^3 of cobalt for particles of approximately 100 A radius. If all particles had the unidirectional torque, the value of E would be 1 dyne-cm/cm^2. Although, as shown below, this is not strictly true, the essential point is that the equivalent exchange torque within the cobalt metal is on the order of $kT_c/4a^2$,

where T_c is the Curie temperature and a the interatomic spacing. This estimate gives about 300 dyne-cm/cm^2 and justifies the assumption that the exchange torque at the interface is less than the torque in the ferromagnetic material. A similar inequality holds for the torque in the antiferromagnetic material.

If we relax the condition that the anisotropy torque in the antiferromagnet be infinite, there is a critical region where the moments in the antiferromagnet undergo discontinuous motions as the moment of the cobalt metal is rotated about by an external field. In this circumstance the uniaxial character is lost and the torque in infinite field has only terms in $\sin 2\theta$ and higher. In addition, there is a rotational hystersis in saturating fields due to the discontinuous reorientation of the moments of the cobaltous oxide. The theory of the rotational hysteresis in single-domain particles[13] shows that for ferromagnetic particles there is rotational hysteresis only if the field is in the range

$$2K \geq HI_s \geq K,$$

and this range the rotational hystersis varies from $1.8K$ to zero. Applying this information to rotational hysteresis in the oxide, we replace the anisotropy of the ferromagnetic material with the anisotropy of the antiferromagnet and for the external field we substitute the exchange interaction across the interface. This yields rotational hystersis in high fields if

$$2K_0[(r_0^3/r^3)-1] \geq \frac{3E}{r} \geq K_0[(r_0^3/r^3)-1],$$

with an average value of

$$\sim K_0[(r_0^3/r^3)-1].$$

Since for our particles half the cobalt is in the oxide (Table I),

$$[(r_0^3/r^3)-1] \sim 2.$$

The rotational hysteresis will therefore be $2K_0$ for those particles that reverse.

Assuming that a volume fraction f of the particles are uniaxial while $(1-f)$ exhibit the rotational hysteresis postulated above, then neglecting the factors of averaging which should strictly be introduced, we have three equations from which we may deduce f, E, and K_0. From the uniaxial torque

$$\frac{3Ef}{r} \doteq 4\times 10^6.$$

From the rotational hysteresis,

$$2K_0(1-f) \doteq 5\times 10^6;$$

and from the fact that rotational hysteresis occurs,

$$2K_0 \doteq 3E/r.$$

The solution of these equations gives

$$f \doteq 0.5,$$

$$E \doteq 2 \text{ dyne-cm/cm}^2 \text{ of interface at } 77°\text{K},$$

$$K_0 \doteq 5\times 10^6 \text{ ergs/cm}^3 \text{ of CoO at } 77°\text{K}.$$

While these figures are very approximate several observations may be made. The first is that the exchange torque across the interface, $3E/r$, is 5×10^6 dyne-cm^3 of cobalt which is of the same order of magnitude as the anisotropy torque in the cobalt.[14] This means that if the anisotropy axes of the cobaltous oxide and cobalt are not coincident, the moment of the cobalt at low temperatures will be deviated substantially from its normal equilibrium position along the c axis as suggested by Roth.[15] An experimental indication of this effect is seen in the data presented in Table I wherein the ratio of remanent magnetization to saturation magnetization with the oxide film is seen to be between 0.80 and 0.90 while if the easy directions were undeviated from the c axis, this ratio would be 0.5 as in the reduced material of column B_1, Table I. Secondly, the large anisotropy in the cobaltous oxide can be compared to the calculations of Kaplan.[16] Using the model of the simple oxides deduced from neutron diffraction observations,[5] Kaplan calculated the dipole-dipole magnetostatic anisotropy to be expected. He found the moments to lie in the (111) sheets of common spin direction while the energy to rotate the magnetization to be perpendicular to the sheet is, for cobaltous oxide, 7×10^6 ergs/cm^3. The anisotropy inferred from the measurements is not to be identified with Kaplan's anisotropy, since his anistropy with its isotropy within the (111) plane could not give rise to a unidirectional effect. Rather we must invoke the usual spin-orbit-lattice coupling which is thought to be the root of anisotropy in ferromagnetics.

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