Magnetic Anisotropy of Cobalt Ferrite ($Co_{1.01}Fe_{2.00}O_{3.62}$) and Nickel Cobalt Ferrite ($Ni_{0.72}Fe_{0.20}Co_{0.08}Fe_2O_4$)*

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A method of measuring the first magnetic anisotropy constant, K_1, of cubic crystals having a large anisotropy was developed which utilized measurements of the torque for directions of the applied field near the direction of easy magnetization. By this method K_1 of a cobalt ferrite crystal was found to be closely approximated by the empirical relationship $K_1=19.6\times10^6 \exp(-1.90\times10^{-5}T^2)$ ergs/cc from 20° to 325°K. Above 325° the measured anisotropy depended upon the length of time the crystal was in the magnetic field. For a nickel cobalt ferrite crystal, K_1, as measured by the usual torque method, was given empirically by $K_1=[8.08 \exp(-3.57\times10^{-5}T^2)-9.78 \exp(-0.863\times10^{-5}T^2)]\times10^4$ ergs/cc from 20° to 600°K while K_2 increased from -4.7×10^4 ergs/cc at 20.5°, passed through zero at 190°, rose to a maximum of 1×10^4 at 280°K, and then above this temperature decreased rapidly to zero. The relationships for K_1 are of the same form as those found by Brükhatov and Kirensky for metallic ferromagnetic materials.

I. INTRODUCTION

THE magnetic properties of single crystals depend on the direction in which they are measured. The anisotropy energy, or magnetocrystalline energy, acts in such a way that the magnetization tends to be directed along certain crystallographic axes called easy directions. For a cubic crystal, such as a ferrite, one can represent the anisotropy energy for an arbitrary direction having direction cosines α_1, α_2, and α_3 referred to the cube edges as

$$E=E_0+K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+K_2(\alpha_1^2\alpha_2^2\alpha_3^2)+\cdots, \quad (1)$$

where K_1 and K_2 are known as the first and second anisotropy constants.

Keffer[1] has recently shown that the temperature dependence of the ferromagnetic anisotropy in cubic crystals is closely related to the degree of correlation between the directions of neighboring spins and that the theories of Van Vleck[2] and Zener[3] can be regarded as limiting cases of no correlation and complete correlation, respectively. These theories yield a relation between K_1 and M of the form

$$K_1(T)/K_1(0)=[M(T)/M(0)]^n, \quad (2)$$

where the magnetization, M, is the appropriate Brillouin value rather than the experimental value. For the limiting case of no correlation, $n=6$, and for the limiting case of complete correlation, $n=10$. In addition, Van Vleck[2] has shown that in a particular case of partial correlation n decreased from 10 to 6 as the temperature is increased from absolute zero.

For ferromagnetic metals having cubic symmetry, the temperature variation of K_1 has been found to follow the empirical Brükhatov-Kirensky[4] relation,

$$K_1(T)/K_1(0)=\exp(-\alpha T^2). \quad (3)$$

This relation follows directly from Eq. (2) if the temperature variation of M is of the frequently observed form, $M(T)/M(0)=(1-aT^2)$, thus:

$$K_1(T)/K_1(0)=(1-aT^2)^n\sim\exp(-naT^2).$$

If the temperature variation of M at low temperatures is of the form $M(T)/M(0)=(1-bT^{\frac{3}{2}})$ as predicted by spin-wave theory, then the corresponding temperature variation of K_1 is

$$K_1(T)/K_1(0)=(1-bT^{\frac{3}{2}})^n\sim\exp(-nbT^{\frac{3}{2}}). \quad (4)$$

It is not possible to distinguish between the above formulas on the basis of presently available data.

The magnetic anisotropy can be measured either by methods utilizing the measurement of static forces or torques or by methods utilizing the measurement of electronic resonance absorption at microwave frequencies. These methods have been shown to yield different values for the magnetic anisotropy for the specific case of nickel ferrite at low temperatures by Bozorth *et al.*[5]

In the present work, measurements of the magnetic anisotropy of a cobalt ferrite ($Co_{1.01}Fe_{2.00}O_{3.62}$) and a nickel cobalt ferrite ($Ni_{0.72}Fe_{0.20}Co_{0.08}Fe_2O_4$) single crystals by static torque methods are presented.

II. APPARATUS AND PROCEDURE

The apparatus used to make these measurements is a torque magnetometer designed so that the torque exerted by the crystal can be measured as a function of

* This work was performed at the U. S. Naval Ordnance Laboratory and was submitted to the University of Maryland in partial fulfillment of the requirements for the Doctor of Philosophy degree in physics.

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[1] F. Keffer, Phys. Rev. **100**, 1692 (1955).

[2] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

[3] C. Zener, Phys. Rev. **96**, 1335 (1954).

[4] N. L. Brükhatov and L. V. Kirensky, Physik. Z. Sowjetunion **12**, 602 (1937) and Tech. Phys. (U.S.S.R.) **5**, 171 (1938).

[5] Bozorth, Cetlin, Galt, Merritt, and Yager, Phys. Rev. **99**, 1898 (1955).

temperature, applied magnetic field, and crystal orientation with respect to the applied field.

The torque, **L**, exerted by a magnetized crystal is given by $-\partial E/\partial\psi$, where ψ is the angle between an arbitrary direction in the plane perpendicular to the torque axis and the projection of **M** onto this plane. For the specific case shown in Fig. 1 where the torque axis is in the [011] direction, **M** is in the (011) plane, and ψ is measured in this plane from the [100] direction, the magnitude of the torque is given by

$$L=-\tfrac{1}{8}K_1(3\sin4\psi+2\sin2\psi) -1/64K_2(\sin2\psi+4\sin4\psi-3\sin6\psi)+\cdots. \quad (5)$$

If the applied field is strong enough to saturate the crystal magnetically, the values of K_1 and K_2 can be found by fitting the observed torque *vs* direction-of-magnetization curve to this equation.

In cases where the applied field is not strong enough to saturate the crystal except in directions near the direction of easy magnetization the following method was developed. The magnetic field, **H**, is applied in the (011) plane and θ, ψ, and ϕ are defined as shown in Fig. 1. For small ψ, Eq. (5) reduces to $L=-2K_1\psi$. The torque exerted by the crystal is given by the equation, $L=-HM\sin\phi$, which for small values of ϕ reduces to $L=-HM\phi$. If A is defined as $-L/\theta$, and since $\theta=\psi+\phi$, it then follows that

$$(1/A)=(1/2K_1)+(1/HM). \quad (6)$$

Thus, at a fixed temperature, K_1 and M can be determined from measurements of L as a function of θ and **H**.

It can be shown[6] for materials having a positive K_1 that, when **H** is in the (011) plane near a [011] direction, it is in general not energetically favorable for **M** also to lie in the (011) plane. This means that this method cannot be used to obtain the value of K_2.

III. SPECIMENS

The chemical analysis[7] of the cobalt ferrite crystal performed on a sample of 50 mg indicated the formula $Co_{1.01}Fe_{2.00}O_{3.62}$ as compared with the ideal $CoFe_2O_4$. None of the other components exceeded 0.05% by weight. The nickel cobalt ferrite crystal was also chemically analyzed,[8] but here the chemical equation $Ni_{0.72}Fe_{0.70}Co_{0.08}Fe_2O_3$ was obtained by assuming that there is an amount of divalent iron present to make the total divalent-trivalent ratio 1 to 2, and also that there is sufficient oxygen to balance the metallic components. If one assumes that the above single crystal spinel is completely inverted and uses $2.2\mu_B$ for Ni^{++}, $4.0\mu_B$ for Fe^{++}, and $3.8\mu_B$ for Co^{++}, a total magnetic moment of $(2.68\pm0.05)\mu_B$ should be expected. This particular sample has been measured by Maxwell[9] and the saturated moment at low temperatures was found to be $(2.63\pm0.03)\mu_B$. The agreement between the magnetic and chemical data gives confidence in the chemical formula.

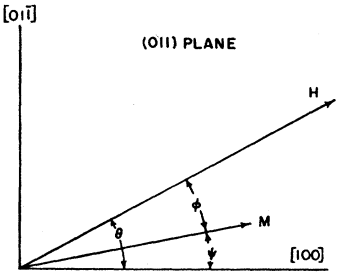

FIG. 1. Relative positions of **H** and **M** vectors in (011) plane.

The crystals were formed into spheres in a Bond-type sphere grinder.[10] Measurements of the diameter and weight of the cobalt ferrite sphere gave a density of 5.33 in comparison to the theoretical density of 5.29 which is based on x-ray measurements. Similarly the measurements of the diameter and weight of the nickel cobalt ferrite sphere yielded a value of 5.27 for its density as compared with a theoretical value of 5.38. The volumes used in the anisotropy calculations, however, are based on volumes calculated from the measured weights and theoretical densities.

After being formed into spheres, the crystals were annealed by heating to 700°C and cooled to room temperature at the rate of about 100°C per hour in a furnace heated with alternating current so that in effect the cooling was done in a small alternating magnetic field.

The crystals were oriented by using back-reflection Laue pictures and were mounted on the support rod with a [110] crystal direction parallel to the direction of the support rod. It is estimated that the orientation of the crystal as mounted on the support rod was within 1 degree of a [110] direction.

IV. RESULTS AND DISCUSSION

The torque on the cobalt ferrite crystal was measured in fields greater than 7500 oersteds and at small angles with the easy direction of magnetization [100]. The plots of $1/A$ *versus* $1/H$, shown in Fig. 2, are linear and with the aid of Eq. (6) K_1 and M can be calculated. The graph of $\log K_1$ *vs* T^2 is shown in Fig. 3 and the M *vs* T curve in Fig. 4. Since $\log K_1$ *versus* T^2 is a straight line up to about 340°K, the measurements can be fitted to the Brükhatov-Kirensky relation. The result is

$$K_1=19.6\times10^6\exp(-1.90\times10^{-5}T^2)\ \text{ergs/cc}.$$

It is interesting to note that below 100°K the data are

[6] H. Shenker, Ph.D. thesis, University of Maryland, 1955, Publication No. 12090 University Microfilms, Ann Arbor, Michigan (unpublished).

[7] Chemical analysis performed by Horace J. Hallowell, Danbury, Connecticut.

[8] Chemical analysis performed by the Naval Gun Factory, Washington, D. C.

[9] T. R. McGuire and L. R. Maxwell, Bull. Am. Phys. Soc. Ser. II, 1, 23 (1956).

[10] W. L. Bond, Rev. Sci. Instr. 22, 344 (1951).

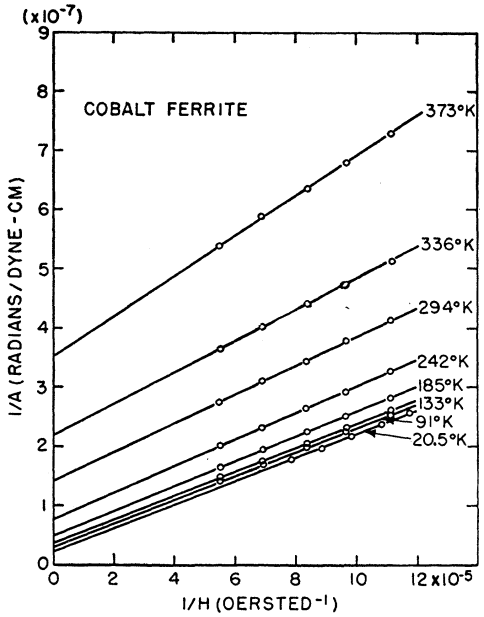

FIG. 2. $1/A$ *vs* $1/H$ curves for cobalt ferrite.

not sufficiently accurate to select between Eq. (3) and Eq. (4).

At temperatures above 425°K the torque depended on the length of time the specimen was in the magnetic field and also upon the crystallographic orientation relative to the magnetic field during the heat treatment. In general the torque values no longer displayed cubic-type symmetry.[11]

The value of the saturation magnetization is in good agreement at 0°K with that obtained by Pauthenet[12] for very pure powdered cobalt ferrite. The differences up to about 325°K may well be due to actual differences in the composition of the material; however, the more rapid falloff above 325° is probably due to a magnetic heat-treatment effect such as found by Bozorth, Tilden,

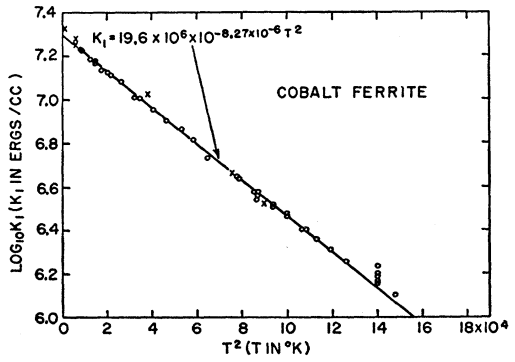

FIG. 3. $\mathrm{Log}_{10}K_1$ as a function of T^2 for cobalt ferrite.

[11] I am grateful to Dr. Bozorth of Bell Telephone Laboratories for informing me of his heat treatment work on cobalt ferrite prior to these measurements.

[12] R. Pauthenet, Ann. phys. [12] **7**, 710 (1952).

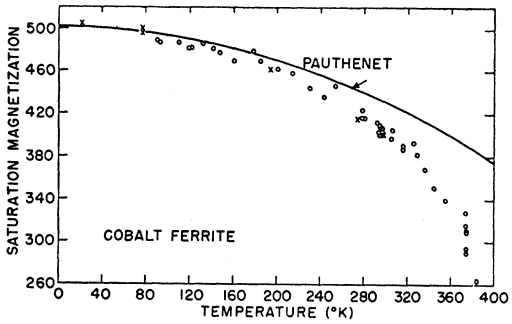

FIG. 4. Magnetic moment (M) as a function of temperature for cobalt ferrite.

and Williams[13] and Williams, Heidenreich, and Nesbitt.[14]

For the nickel cobalt ferrite crystal, measurements of torque were made for the applied field in the (011) plane. It was found that there was a variation of the torque of the order of 3% as the applied field was changed from 7500 to 15 000 oersteds. The torque varied linearly with field strength in this range and the absolute value of the torque increased with increasing field for directions of magnetization between the [111] and the [100] directions, and decreased between the [111] and the [011] directions. Because of this torque variation with field, it was necessary to extrapolate these measurements back to zero magnetic field. The values of K_1 and K_2 obtained from the zero-field data are shown in Fig. 5.

The measured values of K_1 up to 600°K can be fit by the equation

$$K_1=[8.08\exp(-3.57\times10^{-5}T^2)-9.78\exp(-0.863\times10^{-5}T^2)]\times10^4 \text{ ergs/cc.}$$

This equation consists of two terms of the Brükhatov-

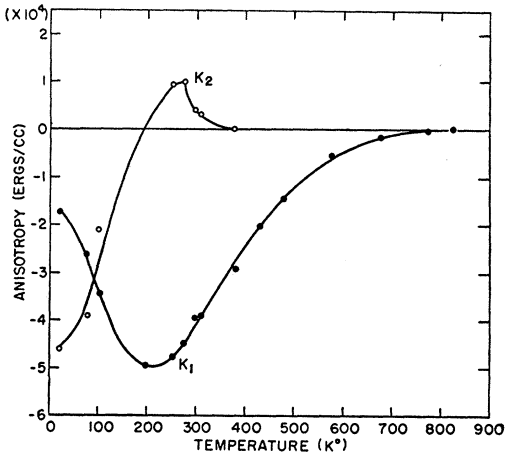

FIG. 5. First (K_1) and second (K_2) anisotropy constants of nickel cobalt ferrite as a function of temperature.

[13] Bozorth, Tilden, and Williams, Phys. Rev. **99**, 1788 (1955).

[14] Williams, Heidenreich, and Nesbitt, J. Appl. Phys. **27**, 85 (1956).

Kirensky type. Preliminary measurements by McGuire[9] of K_1 for this crystal by the microwave resonance method, indicate that the major part, if not all, of the first term represents the difference between the values of K_1 obtained by a static method and that obtained by a microwave method.

Measurements were also made on the crystal after it had been heat treated by cooling slowly in a magnetic field parallel to each of the principal crystallographic directions from 700°C. Generally this heat treatment caused a departure from cubic symmetry of the torque curves and a maximum change in the torque values of about 15%.

Since the theories of ferromagnetic anisotropy have not been explicitly extended to ferrites, it is of interest then that the temperature dependence has the form expected of a ferromagnetic substance. If the experimental values of K_1 and M for the nickel cobalt ferrite crystal are substituted in Eq. (2) the following values of n are obtained: 8 ± 4 at 100°K 8 ± 2 at 200°K, and 8 ± 1 at 300°K.

V. ACKNOWLEDGMENTS

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New Type of Oscillatory Magnetoresistance in Metals*

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The magnetoresistive properties of a thin sodium wire have been studied at 1°K in transverse magnetic fields (H_T) up to 60 000 gauss. This study was undertaken in order to determine whether magnetoresistive oscillations of the de Haas-van Alphen type could be detected in the vicinity of 60 000 gauss. Although no such oscillations were found, the magnetoresistance for H_T below 15 000 gauss exhibited a completely new type of oscillatory phenomena. These new oscillations are periodic in H with a decreasing amplitude in increasing magnetic fields, whereas the de Haas-van Alphen oscillations would be periodic in H^{-1} with an increasing amplitude in increasing magnetic fields. The period of these new oscillations is in excellent agreement with the period of the oscillatory behavior predicted theoretically by Sondheimer for the magnetoresistance due to surface scattering of thin metallic films in H_T. From this period, a value for the electronic momentum was obtained. The significance of these new oscillations is discussed.

INTRODUCTION

IN the study of the electronic energy-band structure of metallic media, de Haas-van Alphen and cyclotron resonance phenomena[1] have proved to be important tools for obtaining some information concerning various electronic parameters and the nature of some parts of the Fermi surface. However, there exists a disappointing gap between the successful experiments which have been performed and tractable theory. Whereas the detailed theory on the one hand is based upon a free-electron model employing simple Fermi surfaces, so that it can best be applied to the Group I metals, the experiments on the other hand have revealed these phenomena only in non-Group I metallic conductors with complicated Fermi surfaces. These phenomena have not as yet been observed in the Group I metals because of the inherent difficulties in establishing the necessary experimental conditions. Since the Group I metal sodium is the closest known approximation to an isotropic free-electron metal, a very careful search was made in this experiment to find the characteristic H^{-1} oscillations of the de Haas-van Alphen[2] type in the magnetoresistance[3] of sodium under reasonably favorable experimental conditions. While no H^{-1} oscillations were found,[4] a new type of magneto-oscillatory behavior stemming from magnetic "size effects" was observed.

The first theoretical analysis using Fermi statistics

* For a preliminary report, see J. Babiskin and P. G. Siebenmann, Bull. Am. Phys. Soc. Ser. II, 2, 140 (1957).

[1] R. G. Chambers, Can. J. Phys. 34, 1395 (1956). A recent review on cyclotron resonance and de Haas-van Alphen phenomena as related to the Fermi surface.

[2] For a recent review article on the de Haas-van Alphen effect, see D. Shoenberg, *Progress in Low Temperature Physics* (North Holland Publishing Company, Amsterdam, 1957), Vol. II, Chap. VIII.

[3] A one-to-one correspondence has been experimentally established between the periods in H^{-1} of both the de Haas-van Alphen effect and of the oscillatory galvanomagnetic and thermomagnetic effects for various non-Group I metals; e.g., see M. C. Steele and J. Babiskin, Phys. Rev. 98, 359 (1955).

[4] Previous unsuccessful attempts to find H^{-1} oscillations in Group I metals have been made in steady magnetic fields up to 32 000 gauss [J. S. Dhillon and D. Shoenberg, Trans. Roy. Soc. (London) 248, 1 (1955)] and in pulsed magnetic fields up to 100 000 gauss [D. Shoenberg, Physica 19, 791 (1953)]; see also reference 2.