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RESEARCH ON SPONTANEOUS MAGNETIZATION IN SOLID BODIES

I.S. Jacobs, D.S. Rodbell, and W.L. Roth

General Electric Research Laboratory

AERONAUTICAL SYSTEMS DIVISION

62-4-1

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February 1962

AERONAUTICAL SYSTEMS DIVISION
AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

FOREWORD

This report covers work carried out in the Metallurgy and Ceramics Research Department of the General Electric Research Laboratory under USAF Contract No. AF-33(616)-7396 entitled "Research on Spontaneous Magnetization in Solid Bodies." This contract was initiated under Project 7371, "Electronic and Magnetic Materials," Task No. 737103, "Magnetic Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology Aeronautical Systems Division, with W.G.D. Frederick acting as project engineer. The guiding theme of the research was the study of fundamental interactions and the microstructure of the internal fields in selected magnetic materials by means of magnetic resonance techniques and high-strength magnetic fields. During the latter part of the contract period, the use of neutron diffraction facilities was introduced, as required, to supplement the research programs in progress under the general work statement.

This Final Report is concerned with the period 1 June 1960 to 31 October 1961. The principal participants in this research were I.S. Jacobs, D.S. Rodbell, and W.L. Roth. The authors would like to acknowledge the continued valuable assistance of P.E. Lawrence throughout this work. Many colleagues also provided frequent stimulation and encouragement. In particular, they wish to acknowledge fruitful association with Prof. R. Street of Monash University, Victoria, Australia, and Dr. W.P. Wolf of the Clarendon Laboratory, Oxford, England, during extended visits to the General Electric Research Laboratory, and also to acknowledge helpful discussions with Dr. M.B. Webb, formerly with the Laboratory, and presently at the University of Wisconsin.

Much of this research was written up for various publications and oral presentations to various international and national Conferences on "Magnetism and Magnetic Materials" in New York; "Magnetism and Crystallography" in Kyoto, Japan; and "High Magnetic Fields," Cambridge, Massachusetts. It is used in this report to describe the work done under this contract.

ABSTRACT

A number of research projects dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials were carried out. (a) The nuclear magnetic resonance of Co^{59} in metallic cobalt powders has been examined. In addition to the absorption characteristic of Co^{59} in face-centered cubic cobalt, there were found an additional group of absorptions, one of which is clearly associated with hexagonal close packed cobalt. (b) The phenomenon of spin-flopping in antiferromagnetic MnF_2, in which the axis of antiferromagnetism is decoupled from the crystal axes, was observed by magnetization measurements in high pulsed magnetic fields. Its position coincided with the value, 93 kOe, predicted from measurements of antiferromagnetic resonance with millimeter microwaves. (c) The temperature dependence of the magnetocrystalline anisotropy of face-centered cubic cobalt metal was examined by ferromagnetic resonance on single crystal thin films and submicron precipitate particles in Cu, at temperatures below the range in which this is the stable structure. Satisfactory agreement is obtained for a tenth power law between anisotropy and magnetization. (d) A very brief review paper on pulsed field magnetization measurements in compounds was prepared. (e) An investigation of magnetic exchange and structure in lanthanum manganite perovskite compounds spanning the transition between antiferromagnetism and ferromagnetism was performed using neutron diffraction and high field magnetization techniques. Evidence favored the single-phase canted spin model for this region over the model of a mixture of two crystallographically similar but magnetically distinct phases. (f) Seven additional exploratory projects were undertaken, some of which hold considerable promise for development.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

Jules I. Wittebort
Chief, Thermophysics Branch
Physics Laboratory
Directorate of Materials and Processes

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RESEARCH ON SPONTANEOUS MAGNETIZATION IN SOLID BODIES

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INTRODUCTION

The work of this project is concerned with fundamental interactions and the microstructure of internal fields in magnetic materials selected from among the ferromagnetic elemental metals of the iron group and the rare earth group, the rare earth garnets and antiferromagnetic oxides and halides. The special tools employed are electron spin and nuclear magnetic resonance, pulsed high magnetic fields (up to 150 kilo-oersteds), and neutron diffraction as required.

The accomplishments associated with this contract fall into several groups. In Group A are included special tasks requested under the contract, or associated with it in a supplementary manner. In Group B are the various research projects conducted in whole or in part under the contract and carried to a state of completion as judged by the preparation of a manuscript for publication. Four papers have been prepared for publication, and one other is included in this group which is nearly complete but lacks a full manuscript at present. The fact that these projects have been completed does not mean that further closely related research is not desirable. In some instances specific recommendations are made as to possible future activity.

Lastly, Group C comprises those projects conducted in an exploratory way, some of which appear quite promising for future development but are still in their initial stages, others of which are still too preliminary for very reliable assessments of their potentialities. Seven projects fall into this group.

GROUP A

1. Special Report

In the Quarterly Progress Report No. 1 under this contract term was included a special report entitled "Introduction to Magnetic Resonance in Solids" and an Annotated Bibliography of significant review articles and research articles in the various fields of magnetic resonance. This Special Report was prepared in fulfillment of a task requested in Exhibit A of the contract. Its contents are not repeated in this Final Report.

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2. Training Visit

During the third quarter of the contract term, Mr. W.G.D. Frederick of the Directorate of Materials and Process, Aeronautical Systems Div., USAF, spent the week of February 6-10, 1961, visiting the General Electric Research Laboratory. By prior arrangement this period was utilized to provide an introduction to the methods of measurement and analysis generally employed in microwave resonance spectroscopy.

3. Table of Magnetization Behavior in High Magnetic Fields

A project outside the scope of this contract, but of supplementary interest to the reader of this report is the preparation of a brief table and text on the information obtained by high field studies on magnetic materials. This was submitted as a contribution to the section on "Magnetic Properties of Materials" in the American Institute of Physics Handbook. It is included in this report as Appendix A.

GROUP B

1. The Nuclear Magnetic Resonance of Co^{59} in Metallic Cobalt Powders

The nuclear magnetic resonance of Co^{59} in metallic cobalt powders has been examined. In addition to the absorption characteristic of Co^{59} in face-centered cubic cobalt, we find an additional group of absorptions. The identification of one of these (located 10 Mc/s above the f.c.c. resonance absorption) as arising from Co^{59} nuclei in hexagonal-close-packed cobalt has been made by using both magnetic resonance and standard x-ray identification methods on samples that have been subjected to a variety of treatments. By these treatments the relative fraction of a given sample, that is, h.c.p., can be changed and the identification is made on that basis. There are two other resonance lines that lie intermediate in frequency between the f.c.c. (213.1 Mc/s at 25°C) and the h.c.p. line. The identification of these resonances has not yet been fully established. The work described above was published in the Physical Review, <u>121</u>, 84 (1961).

THE NMR SPECTRUM OF Co^{59} IN METALLIC COBALT POWDERS

We have examined the nuclear magnetic resonance of Co^{59} in finely divided cobalt metal samples. The spectrum contains several lines in addition to the already well known nuclear resonance of f.c.c. cobalt. The method of observation was similar to that described by Gossard and Portis[1,2] who first observed the resonance for f.c.c. cobalt. The transmission of a frequency modulated signal through a coaxial line, packed with the powder sample, is displayed on a cathode ray tube. The resonance absorption modifies the transmission when the frequency corresponds to the nuclear resonant frequency. For some powder samples, the oxide coating* on the individual particles was sufficient to provide the requisite electrical insulation; in other cases the particles were wax coated by wetting the powders with a solution of paraffin wax in benzene and drying under vacuum. The relative proportions of cubic and hexagonal phases in the powder samples were determined from x-ray patterns measured with a proportional counter spectrometer and CrK_α radiation.

The NMR traces obtained with a commercially available sample of cobalt† at 300° and 77°K are shown in Figs. 1(a) and (b), respectively. Part (c) of the figure is an index to prominent parts of the spectrum. The frequencies 1 and 2 associated with the main resonance are approximately 0.5 Mc/s lower than those reported by Portis and Gossard;[2] however, this difference depends upon frequency sweep rate; for very slow sweep rates there is no discrepancy. We note that the line shape also depends upon sweep rate.

The following observations established that the lowest resonance (frequencies 1 and 2) and the highest resonance (frequencies 5 and 6) are to be associated with the f.c.c. and h.c.p. phases, respectively. Figure 2(a) was obtained with a different sample** of cobalt powder than that used for Fig. 1. X-ray analysis showed that the ratio of h.c.p./f.c.c. for the sample of Fig. 2 was 0.19, whereas for the powder sample of Fig. 1, the ratio was 1.38. The spectrum of MCB powder, taken with identical apparatus settings, is included for comparison in Fig. 2(b). The reduction of the h.c.p./f.c.c. ratio is accompanied by a decrease in the intensity of the highest frequency resonance.

To confirm the identification of the NMR resonances, the relative proportion of h.c.p. phase in the MCB cobalt was increased by col.-working the powder.[3] The MCB powder was compressed at 80,000 psi into briquettes which were then powdered and annealed for 2 hours at 300°C; the spectrum in Fig. 3(b) was then obtained. The decrease signal intensity required a higher gain setting than the previous data. A trace of the untreated MCB powder, 3(a), is included

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*The spectra of a powder sample before and after removal of the oxide by heating in a current of dry hydrogen were identical.

†Obtained from Matheson, Coleman, and Bell (-325 mesh).

**Fisher Scientific Company.

(a)

(b)

TRANSMITTED POWER

(c)
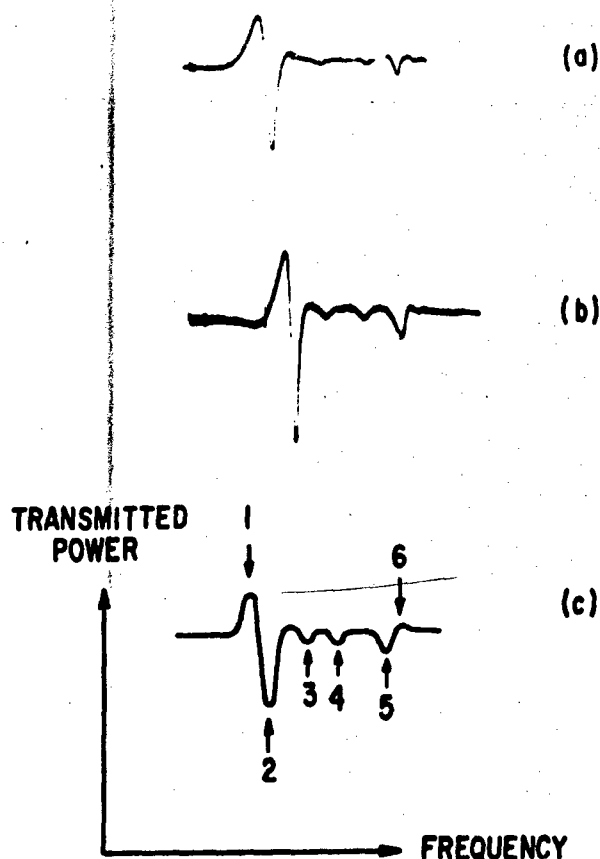
FREQUENCY

Fig. 1 The nuclear resonance spectrum of cobalt in metallic powders (Matheson, Coleman, and Bell, -325 mesh). The figure displays transmitted power vs frequency. The peak to peak variation of the largest signal is 5 per cent of the average transmitted power; (a) is the spectrum at room temperature (300°K); (b) is the spectrum at liquid nitrogen temperature (77°K); (c) is the index to the frequencies tabulated below.

	Frequency Mc/s	
Position	300°K	77°K
1	211.8_4	215.4_0
2	212.9_7	216.8_3
3	215.4_3	219.8_7
4	218.1_7	223.3_0
5	220.8_0	226.8_7
6	221.9_9	227.9_3

We note without explanation that the shift in resonance frequencies between 300° and 77°K is linear with frequency.
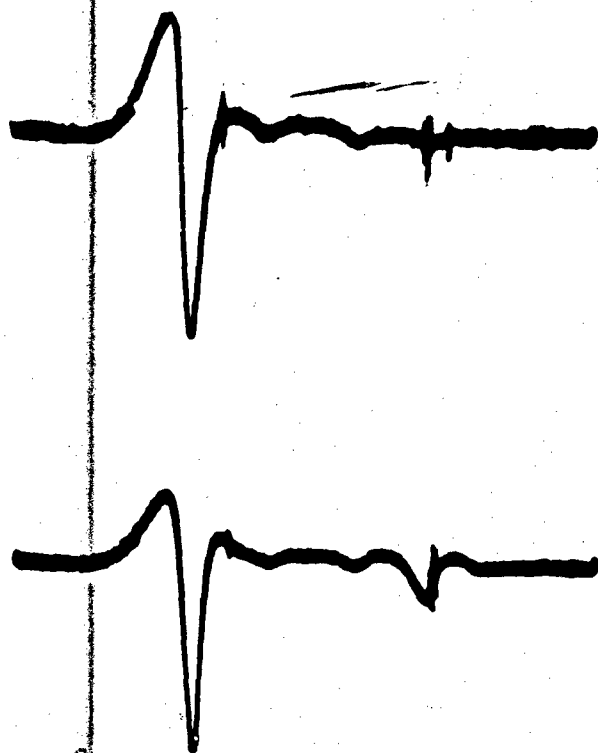
(a)

Fig. 2 (a) is the room temperature spectrum of a fine grained powder sample of metallic cobalt (Fisher Scientific Company) which has an h.c.p./f.c.c. ratio of 0.19 as determined by x-ray analysis; (b) is the room temperature spectrum of the MCB sample in which the h.c.p./f.c.c. ratio is 1.38.

(b)

4

(a)

(b)
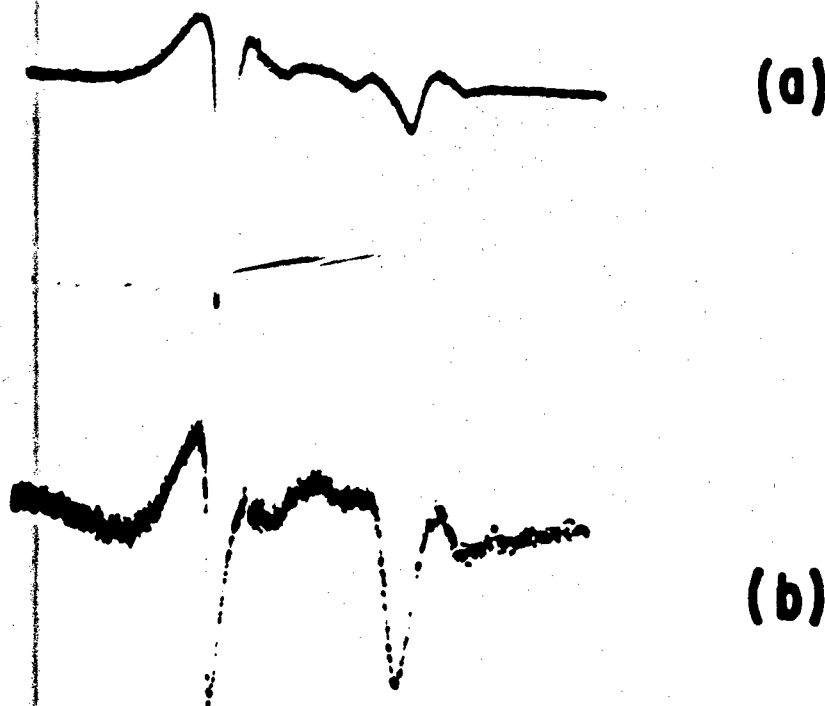
Fig. 3 (a) is the room temperature MCB sample spectrum; (b) is the same sample after a deformation and heat treatment that converted sufficient f.c.c.→h.c.p. to give an x-ray determined h.c.p./f.c.c. ratio of 4.9.

for comparison. The intensity of the highest frequency resonance has increase relative to the lowest frequency resonance. The h.c.p./f.c.c. ratio for the cold-worked cobalt has increased to 4.9. We therefore conclude from the data presented here that the lower and higher frequency resonances are associated with the f.c.c. and h.c.p. phases of cobalt, respectively. We understand* that Professor Y. Koi, Tokushima University, and Dr. W. Hardy, IBM Laboratories, Owego, New York, have both observed a second resonance very similar to that we report here as associated with the h.c.p. phase.

In considering the relative intensities of the resonances of the f.c.c. and h.c.p. phases and allowing for the x-ray determined volume fractions of these constituents, we note that the h.c.p. resonance is weaker by almost an order of magnitude than that of the f.c.c. phase. We believe that the relative weakness of the h.c.p. resonance derives from the interaction of the nuclear quadruple moment of the Co^{59} nucleus with the noncubic crystalline field of the h.c.p. phase. In a crystalline electric field of cubic symmetry the Co^{59} nucleus ($I = 7/2$), subject to a strong hyperfine field, H_{eff}, has ($2I + 1$) distinct energy levels which are equally spaced by $\Delta = g_N \beta_N H_{eff}$. However, in a noncubic crystalline field, there is an electric field gradient at the nucleus that interacts with the nuclear quadruple moment. The quadrupolar interaction shifts the energy levels and only

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*A. Portis, private communication.

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the transition $-1/2 \rightarrow +1/2$ is still given by Δ.* The other transitions are shifted to higher or lower frequencies dependent upon the relative orientation of the crystalline field gradient and the effective magnetic field. The order of magnitude of these shifts may be as much as 20 Mc/s which value is observed for the Co nucleus in CoF_2.[5] We recognize that this comparison of electric field gradients between CoF_2 and cobalt metal is by no means justified, and we quote the value here simply for illustration. In addition to the shift of the energy levels caused by the noncubic crystalline environment the relative orientations of the local effective hyperfine field are randomized by the domain walls that "drive" the resonance. Within the domain walls the effective magnetic field scans all directions between the positive and negative "c" axes and this randomization broadens all but the $-1/2 \rightarrow +1/2$ resonance line because of the anisotropy of the energy levels. Consideration of the transition probabilities shows that the relative intensity of absorption from just the $-1/2 \rightarrow +1/2$ transition is 4/21. We thus expect that the h.c.p. cobalt resonance intensity should be, on the above considerations, 20 per cent of the intensity associated with an equal volume of f.c.c. cobalt.

From the relative positions in frequency of the resonances, we note that H_{eff} for the h.c.p. phase is 5 per cent higher than for the f.c.c. phase. The various contributions to H_{eff} have been discussed,[2] and it is clear that small changes in the contributing terms could account for the magnitude of the difference observed. A proper calculation of this point seems lacking to date.

The origin of the smaller resonances at frequencies 3 and 4 has not yet been determined, but it is tentatively suggested that they are associated with stacking faults. Both growth and deformation faults are observed in hexagonal cobalt.[3] Growth faults are sequences of three planes, and deformation faults are sequences of four planes of cubic close packing within the hexagonal phase. If the identification of the smaller resonances with faulted material is correct, the resonance at frequency 3, nearer the f.c.c. absorption, probably is associated with deformation faults; whereas, the resonance at frequency 4, nearer the hexagonal absorption line, is associated with growth faults. These possibilities are currently being investigated.

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*This statement is correct only to 1st order perturbations. In the second order treatment there is an additional shift, but more important, there is also a broadening of the levels. For an analogous effect in electron spin resonance, see Ref. 4.

2. Spin-Flopping in MnF$_2$ in High Magnetic Fields

We give here a discussion of the background of this experiment. In a simple antiferromagnet the magnetic moments, or simply "spins," are arranged into two groups or "sublattices" which are antiparallel to each other and distributed in a periodic way. The axis of the antiferromagnetism is that collinear with these antiparallel spin sublattices. If a magnetic field is applied perpendicular to this axis, the spin directions deviate from their original positions by an amount proportional to the field and given by the perpendicular susceptibility, $\chi_\perp$. This is a relatively easy process inasmuch as the field exerts a large torque on each of the spins, the deviations occurring against the exchange energy, or its equivalent field H_E, responsible for the antiferromagnetism. (Note: $H_E \simeq M/\chi_\perp$ where M is the spontaneous moment of one sublattice.) On the other hand, if the magnetic field is applied parallel to the axis of antiferromagnetism the situation is quite different, particularly at temperatures well below the magnetic ordering temperature, or Néel point. The torques from the field on the spins are now zero, or nearly so, although one of the spin sublattices is energetically unfavorably oriented with respect to the field. At 0°K there is no deviation of the spin groups from their original position; i.e., the parallel susceptibility, $\chi_\parallel$, is zero. At higher temperatures this susceptibility is nonzero, rising to meet $\chi_\perp$ at the Néel temperature. Over this same temperature range $\chi_\perp$ is usually constant.

Under these circumstances the spin sublattices of an antiferromagnet would be aligned perpendicularly to an applied magnetic field, for by this means the largest net moment would be induced, and hence the lowest energy would be achieved. An important restraint on this tendency is the presence of a magneto-crystalline anisotropy; i.e., a tendency for the spin systems to favor certain crystallographic directions at the expense of others. This may be characterized by an "effective anisotropy field," H_A, equal to the ratio of the anisotropy energy density K to the sublattice spontaneous moment M. With this restraint, a compromise is reached so that when the field is applied parallel to the easy axis of the anti-ferromagnetic spins, a critical field is required before any significant moment is induced. When this field is attained, the spin sublattices rotate rather abruptly to be nearly perpendicular to the field, and to have the moment induced corresponding approximately to that given by $\chi_\perp$ and the applied field. This somewhat dramatic spin-flopping was predicted and calculated by Néel[6] in 1936 in one of the earliest papers to deal with antiferromagnetism. In our terminology, the value of this critical field is approximately given by $H_c = (2H_E H_A)^{1/2}$. The significance of this type of measurement is that it fixes the value of H_A, in that H_E may be found independently from the value of $\chi_\perp$.

SPIN-FLOPPING IN MnF$_2$ BY HIGH MAGNETIC FIELDS

Néel, in an early study of antiferromagnetism,[6] predicted the magnetic field conditions under which an antiferromagnet would show an abrupt decoupling between the direction of antiferromagnetism and the easy axis. This effect has also been termed "spin-flopping" or "magnetization turnover." He later[7] extended this analysis to behavior termed metamagnetic in which an antiferromagnet abruptly transforms to a fully aligned ferromagnetic array at a critical field. Interest in both phenomena has been considerable.

Spin-flopping, of interest herein, occurs when the magnetic field applied along the easy axis exceeds a critical value. The antiparallel magnetizations of the two sublattices (assumed) turn from the direction of the easy axis to that perpendicular thereto, and incline toward the field direction, producing a sharp increase in net magnetization. The critical field at temperatures well below the Néel point is given approximately by the geometric mean of the exchange field H_E and the anisotropy field H_A, or $H_C \simeq (2H_E H_A)^{1/2}$. The value of H_E may be estimated as the ratio of sublattice magnetization to perpendicular susceptibility, while H_A is the ratio of anisotropy energy density to sublattice magnetization. In detail one finds at any temperature below the Néel point, [6, 8-11] $H_C = [(2H_E + H_A) H_A / (1-\alpha)]^{1/2}$, where α is the ratio of the parallel susceptibility to the perpendicular one.

The first observations of spin-flopping were by Gorter et al.[10] in salts with low Néel temperatures and hence low H_E values. Other observations[12] by Koehler et al., using neutron diffraction, are in compounds with low anisotropy such that decoupling is equivalent to domain rotation.

An equally powerful tool to obtain the same interaction parameters is antiferromagnetic resonance.[13-15] The condition is approximately given by $\omega/\gamma \simeq [2H_E H_A]^{1/2} \pm H$, where ω is the applied frequency, γ the magnetomechanical ratio, and H the applied field. The resonance may be observed in zero applied field typically using millimeter microwaves[16] or far infrared radiation, [17] or it may be tuned to fixed wavelengths in the microwave range using a large field.[18] The present technique of observing the spin-flop magnetization change may be viewed as a "zero-frequency resonance."

MnF$_2$ was selected herein because of the wealth of prior experimental information, which derives in part from its simple electronic configuration, and its close approximation to the two sublattice model of antiferromagnetism. The same reasons have made MnF$_2$ attractive to theoretical study. Its Néel point is 68°K and its magnetic structure is body-centered tetragonal with spin directions along the c-axis.

Magnetization measurements were made in pulsed fields to 140 kOe as previously described.[19] One sample was of pressed powder and a single crystal sample was made available through the courtesy of Dr. J.W. Nielsen of the Bell Telephone Laboratories. In a polarizing microscope a number of subgrains were observed in the crystal, differing in orientation by a degree or so.

Measurements at 77°K were convenient for calibration. On the powder sample, the observed linear magnetization curve corresponded to a susceptibility in agreement (± 3 per cent) with published values.[11, 18b] On the crystal, because of the near equality of parallel and perpendicular susceptibilities[20] at 77°K, this measurement determined the magnetization scale. It also coincided[18b] with the magnetization expected perpendicular to the c-axis at 4.2°K, which was not measured in this investigation.

The magnetization curve for powder at 4.2°K is shown in Fig. 4 where its low field behavior agrees with initial powder susceptibility. It deviates smoothly with increasing field, and approaches the line expected for the perpendicular magnetization curve. Data points were read for both decreasing and increasing fields. Their superposition precludes mechanical rotation of the powder grains. This behavior for a powder was predicted by Néel,[6] but it is clear that it is poorly suited for an estimate of the critical field.

Low-temperature magnetization curves on the crystal were observed first with the c-axis about 7.5° away from the field direction and subsequently with improved orientation to minimize misalignment. The rather abrupt spin-flopping is clearly visible in each case as shown in Fig. 4 for 4.2°K. The data plotted are selected for clarity of presentation from the full reduction of the photographs, read every 4 kOe, using an optical projection system. Measurement at 20.4°K with the poorer orientation gave a curve nearly identical to that at 4.2°K, except for rounding before the spin-flop corresponding to the nonzero value of the parallel suscep-tibility at 20.4°K. No significant hysteresis[7] is observed in the spin-flopping, beyond the experimental scatter. If present, it does not exceed 1 kOe.

If the field were applied exactly along the c-axis of the crystal, a dis-continuous jump in the magnetization would be expected at the critical field. For slight misorientations, the magnetization increase is steep but continuous, and the critical field is closely given by that field for which the nearly aligned curve has half the magnetization of the curve corresponding to the perpendicular orientation. From Néel's plot[6, 7] of the susceptibility-field-orientation relation, a small correction to this midpoint criterion is needed as the misalignment increases. For 7.5° misorientation the field at the midpoint should be increased by 2 per cent to obtain H_C. From these two orientations the average value of H_C is 93 ± 2 kOe.

The solid curves in Fig. 1 are those predicted for misalignments, θ_H, of 7.5° and 2.5°. They are calculated from a simplification of equations previously derived.[6, 11] This simplification neglects the midpoint correction. The solid
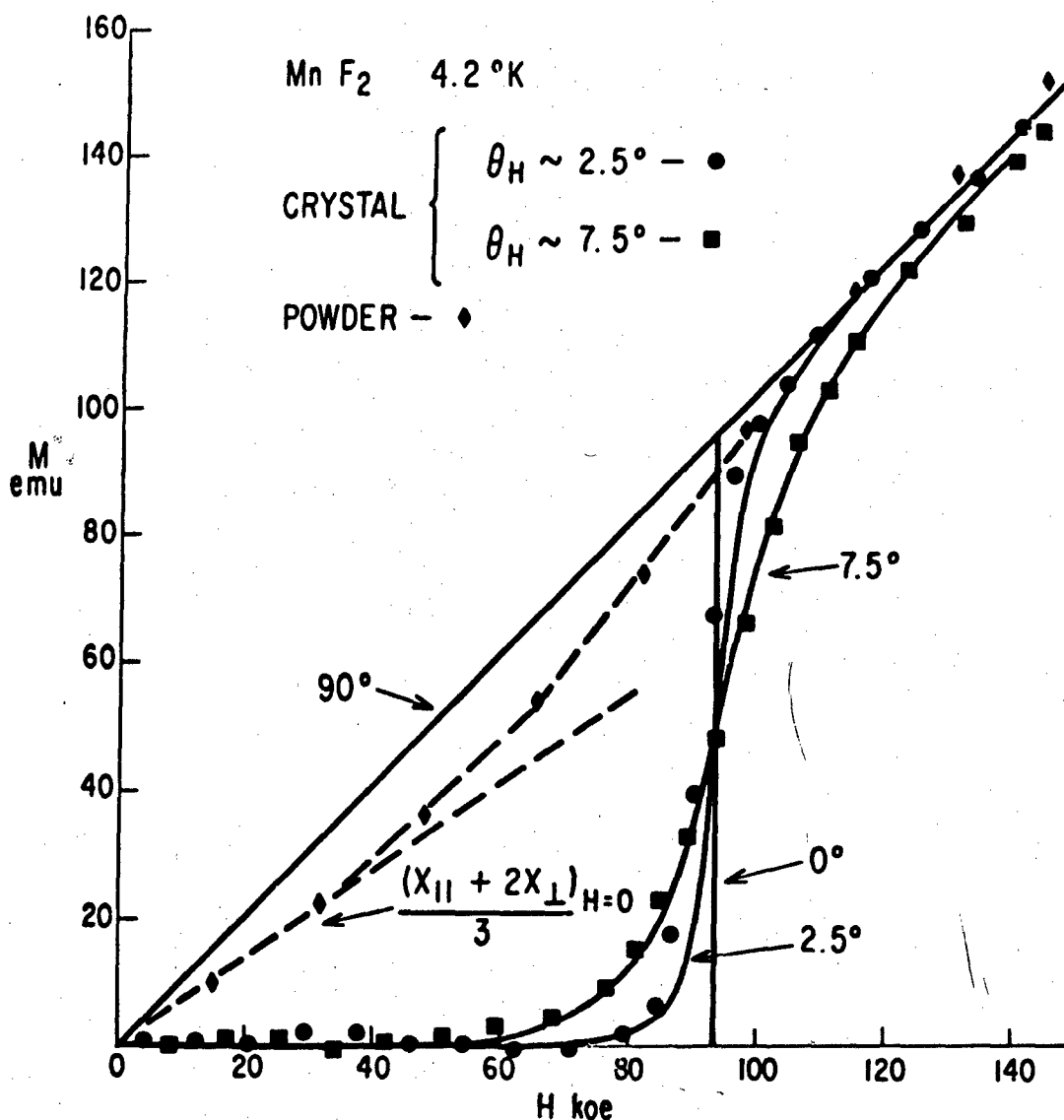
Fig. 4 Magnetization data for powder and various crystal orientations.
Solid curves calculated from simplified theory.

curves are normalized with $H_C = 93$ kOe and $\chi_\perp = 1.03 \times 10^{-3}$ per cc.[21] The better orientation corresponds to about 2.5° misalignment, of which part is embraced by subgrain misorientation.

The critical field value obtained herein is in excellent agreement with values found by microwave resonance by Foner[18] and by Johnson and Nethercot.[16] These had a close connection to theoretical calculations of Keffer[22] and Oguchi.[23] This example demonstrates that magnetization measurements of spin-flopping can be used as an alternative tool to explore interaction energies in antiferromagnets. Choice of technique may depend upon anticipated interaction strengths and magnetic structure.

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At the Conference several interesting points came up in conversations and session discussion about this work. Dr. S. Foner of MIT Lincoln Laboratory pointed out that in compounds with short relaxation times the measurement of $(2H_E H_A)^{1/2}$ by antiferromagnetic resonance techniques might fail, but that the spin-flop measurement might still be possible. Conversely, Prof. A.M. Portis of the University of California (Berkeley) raised a question as to the nature of the spin-flop transition. This led to a discussion of the possible role of antiferromagnetic domain walls as nucleating centers for the transition, and to the possibility of detecting a lag in the transition if the field were to be applied faster than the wall could propagate the high field spin configuration. Inasmuch as R.W. DeBlois[24] of our Laboratory has developed techniques for producing 100 kOe fields about a 1000 times faster than the pulses employed in this work, and for detecting transitions similar to this spin-flop, it is hoped that these possibilities can be investigated further.

Calculations show that an intrinsic hysteresis may be expected in the amount of 2.5 to 3.0 kOe centered about the critical field of 93 kOe. This follows from the formulations of Néel[7] and of Nagamiya, Yosida, and Kubo.[11] However, this hysteresis could be reduced by nucleation at antiferromagnetic domain walls. (For a brief discussion of such walls, see Ref. 25.) The hysteresis here calculated is for a perfectly aligned crystal, i.e., H parallel to the c-axis. Intuitive arguments by C.P. Bean suggest that the hysteresis would be sharply angle-dependent. At present these arguments have not been reduced to a rigorous derivation.

It is planned to look for the hysteresis more carefully with a current-field detection system which is not subject to any suspicion regarding possible "instrumental hysteresis," as is the RC integrator in the present field display. The sample available for this is the 2.5° "misoriented" one which gave the sharpest spin-flop transition. In the technique of R.W. DeBlois, in which the large fields are produced extremely rapidly, the problem of accurately controlling the sample orientation is rather serious. Consequently, some better understanding of either an experimental or a theoretical nature is desired as a guide.

One kind of experimental guide on the possibility of detecting hysteresis has appeared in the very recent work of P.S. Pershan[26] of Harvard. In that paper the nuclear resonance at 160 Mc/sec of F^{19} nuclei is studied in a single crystal of MnF_2 in the presence of a [110] oriented d-c electric field and an [001] oriented d-c magnetic field. The nature of the splitting of the resonance enables the author to conclude that the crystal is nearly one single domain. To the extent that this conclusion is correct, we may be encouraged in the possibility of detecting hysteresis, in that the nucleation centers for the spin-flop are removed. In fact, however, Pershan's technique would be unable to detect domain walls caused by partial dislocations or certain antiphase boundaries and hence some potential nucleating centers may still be possible.

A second point, noted at the Conference, but one which is rather harder to realize in practice, was raised by Dr. R.G. Shulman of the Bell Telephone

Laboratories, who remarked that MnF_2, above the critical field, would have a spin configuration which permitted a slight canting to produce a small net moment (weak ferromagnetism) in the basal plane. This follows from the theoretical work of Dzialoshiskii[27] and of Moriya[28] as applied to NiF_2. The latter compound has the same crystal structure as MnF_2, but at zero field the spin directions in NiF_2 are in the basal plane, while those in MnF_2 are perpendicular thereto. Above the critical field, the spins in MnF_2 lie near to the basal plane.

3. The Magnetocrystalline Anisotropy of Face-Centered Cubic Cobalt Metal

Bulk cobalt has the face-centered cubic crystal structure at temperatures above 390°C, but transforms martensitically to the hexagonal-close-packed modification below that temperature; thus bulk single crystals at temperatures below 390°C are h.c.p. In this investigation we wish to examine f.c.c. cobalt at temperatures below this transformation and do so by employing

(a) single crystal thin films of cobalt--epitaxially deposited onto single crystalline MgO substrates, and

(b) examining the cobalt-rich f.c.c. precipitate in single crystals of 2 per cent cobalt-copper alloys.

The magnetocrystalline anisotropy constants K_1 and K_2 have been determined for face-centered cubic cobalt metal in the temperature range below and through the stability limit of face-centered cubic cobalt in bulk form. The recent and intense interest in the nuclear magnetic resonance of cobalt in finely powdered form--much of which is of f.c.c. structure--has focused attention upon the limited data available for this material. The importance of the magnetocrystalline anisotropy constants arises because the thickness of domain walls in polydomain material and the rotational susceptibility in single-domain material both are dependent upon the magnetocrystalline anisotropy, and these factors are of importance in understanding the intensity of the nuclear magnetic resonance absorptions that are observed in the nuclear resonance experiments. Aside from the immediate interest noted above, the fundamental questions concerning the origin of magnetocrystalline anisotropy and its dependence upon temperature are problems of current interest in the physics of magnetism.

(This research was presented orally at the International Conference on Magnetism and Crystallography held in Kyoto, Japan, during September 25-30, 1961, and will be published in the Conference Proceedings as a Supplement to the Journal of the Physical Society of Japan. It was again presented at the Conference of Magnetism and Magnetic Materials held in Phoenix, Arizona, during November 13-15, 1961.)

THE TEMPERATURE DEPENDENCE
OF THE MAGNETOCRYSTALLINE ANISOTROPY
OF FACE-CENTERED CUBIC COBALT

The magnetocrystalline anisotropy reflects the spatial symmetry of the crystal structure that it is associated with; that is, the spatial dependence of the magnetization energy is intimately connected with the crystal symmetry of the sample. In addition, the temperature dependence of the magnetocrystalline anisotropy is also influenced by the crystal symmetry. The reason for the latter effect may be thought of arising from the fact that, at temperatures greater than absolute zero, the magnetization locally deviates from its equilibrium direction and scans the surrounding spatial orientations giving rise to an averaging of the local anisotropies, that average in an observable value and since it depends on local values also reflects the crystal symmetry. The detailed theory of this behavior is to be found in the literature. [29-32] The general results obtained for cubic crystals are stated as

$$\frac{K_n(T)}{K_n(0)} = \left[\frac{M(T)}{M(0)}\right]^{p_n} \tag{1}$$

with $n = 1$, 2 and $p_1 \doteq 10$, $p_2 \doteq 21$; the "approximately" for the exponent arises from a thermal expansion correction. [33]

The determination of magnetocrystalline anisotropy by ferromagnetic resonance is a relatively standard technique by which we have determined the equivalent "anisotropy fields" K_1/M, K_2/M from an analysis of the applied d-c magnetic field required for resonance as a function of orientation of the single crystal samples. The spectroscopic splitting factor, g, is also determined from the analysis given in the Appendix B and is found to be 2.06 ± 0.03 independent of temperature from 4.2° to 850°K. The measurements are at 9 kMc/s.

In Fig. 5 are presented the primary results of this investigation, the temperature dependence of K_1/M for (a) samples of cobalt precipitated in Cu-2 per cent Co single crystals* and (b) single crystals of cobalt in the form of thin films evaporated onto MgO single-crystal substrates.† The precipitated particles

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*Made available by J.D. Livingston.

†Made available by M.V. Doyle.
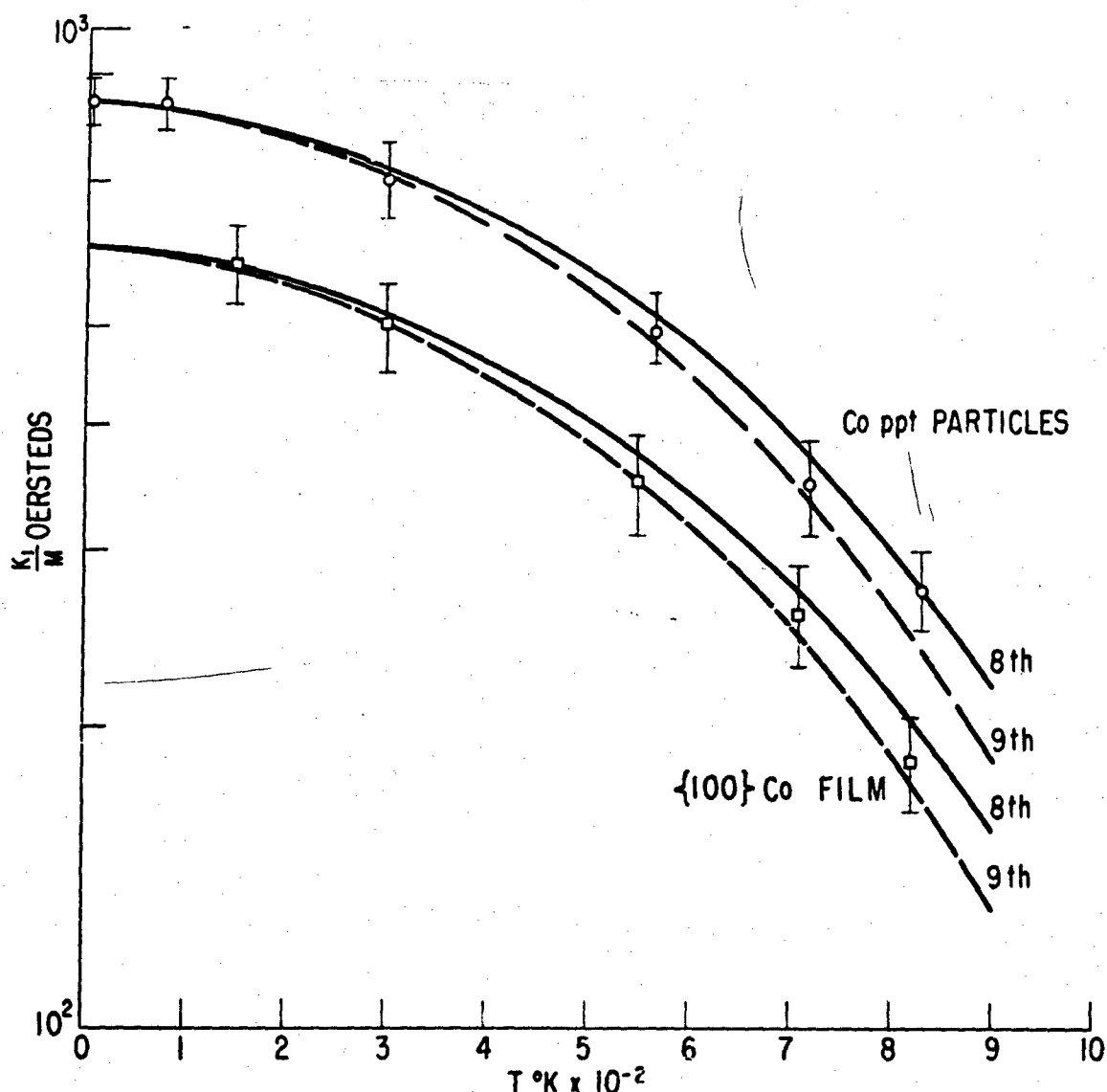
Fig. 5 The temperature dependence of the magnetocrystalline
anisotropy "field" K_1/M for f.c.c. cobalt. The specimen marked $\bigcirc$
corresponds to the cobalt-rich precipitate particles in single crystal
alloys of copper-2 per cent cobalt; the particles have average radii
of 150 A. The specimen marked $\square$ corresponds to a (100) plane
evaporated film 6000 A thick on a MgO single-crystal substrate.
The power law comparison with the nuclear resonance data of
Jaccarino is made for $(p_1 - 1) = 9$ and 8 in each case and normalized
to the data at low temperatures.

of (a) have previously been determined[34] to be of face-centered cubic crystal
structure and essentially spherical in shape; the lattice parameter of these
particles is estimated to be 1.5 per cent larger than bulk f.c.c. cobalt and, in

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addition, they contain about 10 per cent copper. The single crystals (b) are determined by x-rays to be f.c.c. and of a lattice parameter equal to that of bulk f.c.c.

The theories that yield for K_1 a 10th power dependence are primarily developed for a torque determined anisotropy. While there is no difference between torque measurements of anisotropy and the ferromagnetic resonance determined values at absolute zero, this same statement cannot be arbitrarily made at elevated temperatures and in at least one case has been shown to be false.[35] Lacking a better theory we assume a 10th power law to hold.

Since we measure K/M rather than K, the relation (1) should be recast as:

$$\frac{K_n(T)/M(T)}{K_n(0)/M(0)} = \left[\frac{M(T)}{M(0)}\right]^{(p_n-1)} \tag{2}$$

Magnetocrystalline anisotropy may be viewed as a local property and there is some evidence for this even in the case of metals.[36] This view would suggest that σ, the moment per gram (ultimately per atom), rather than M, the moment per cm^3 is of fundamental importance since the number M is diluted by thermal expansion directly [in addition to the correction by Carr[33] that modifies the exponent p]. Because of the above, we shall compare our data with the prediction of:

$$\frac{K_1(T)/M(T)}{K_1(0)/M(0)} = \left[\frac{\sigma(T)}{\sigma(0)}\right]^{(p_1-1)} \tag{3}$$

Since the nuclear resonance frequency of a ferromagnet measures the product of σ with a coupling constant A we have taken Jaccarino's determination[37] of the nuclear resonance frequency vs temperature to be a measure of σ. It is known that for iron the coupling constant A of the nuclear resonance is explicitly temperature dependent.[38] We shall see to what extent a similar situation exists in cobalt.

The exponent is taken (after Carr) to be:

$$p_1 = 10 - \frac{\kappa \omega(T)}{aT^{3/2}}$$

where

$$\kappa = \frac{1}{K_1}\frac{\partial K_1}{\partial \omega} - \frac{10}{\sigma}\frac{\partial \sigma}{\partial \omega}$$

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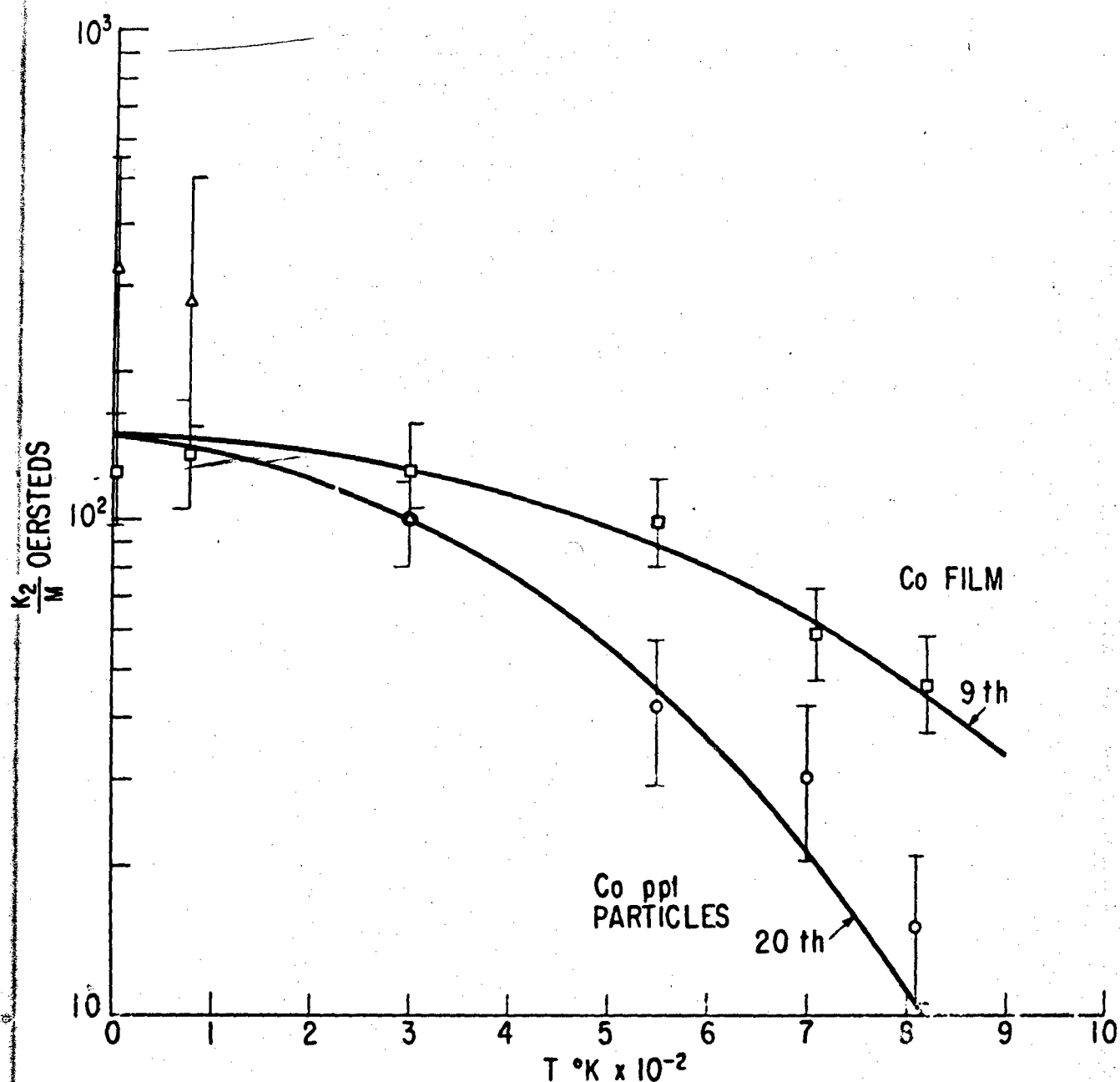
Fig. 6 The temperature dependence of the magnetocrystalline anisotropy field
K_2/M for f.c.c. cobalt. Two samples of cobalt particles are included, one
marked Δ is oriented so that a (110) plane is exposed to observation while one
marked O exposes a (111) plane. The former contains primary information
about K_1/M and secondary information about K_2/M, while this is reversed in
the latter sample. The (111) Co film sample indicated was a film 1000 A
thick evaporated onto a MgO single-crystal substrate. The power law is drawn
to correspond to the data at 300°K.

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is the strain dependence of the magnetocrystalline anisotropy, ω is the strain, and a is the coefficient of the $T^{3/2}$ law describing the magnetization falloff with the temperature T ($a = 3.3 \times 10^{-6}$ °$K^{-3/2}$ from the fit of Jaccarino's data). We estimate κ from the difference between our two types of samples and the difference in their lattice parameters. Neglecting $(10/\sigma)(\partial\sigma/\partial\omega)$ we find that $\kappa \simeq 4.1$ and is temperature independent. We take ω $(T) T^{-3/2}$ to be $\sim 10^{-6}$ (as for iron and nickel above 300°K) and obtain:

$$(p_1 - 1) = 9 - \frac{4.1 \times 10^{-6}}{3.3 \times 10^{-6}} = 7.8 \quad .$$

The data of Fig. 5 are in agreement with Eq. (3) using our estimate above for p_1. Notice that at low temperatures better agreement is obtained with higher powers of p_1, i.e., $p_1 - 1 = 9$, whereas at high temperatures $p_1 - 1 = 8$. This probably reflects the fact that $\omega T^{-3/2}$ is not temperature independent.

The data obtained for K_2/M by our experiment are shown in Fig. 6, and we remark first that the limits of error are broader in this case; and although the
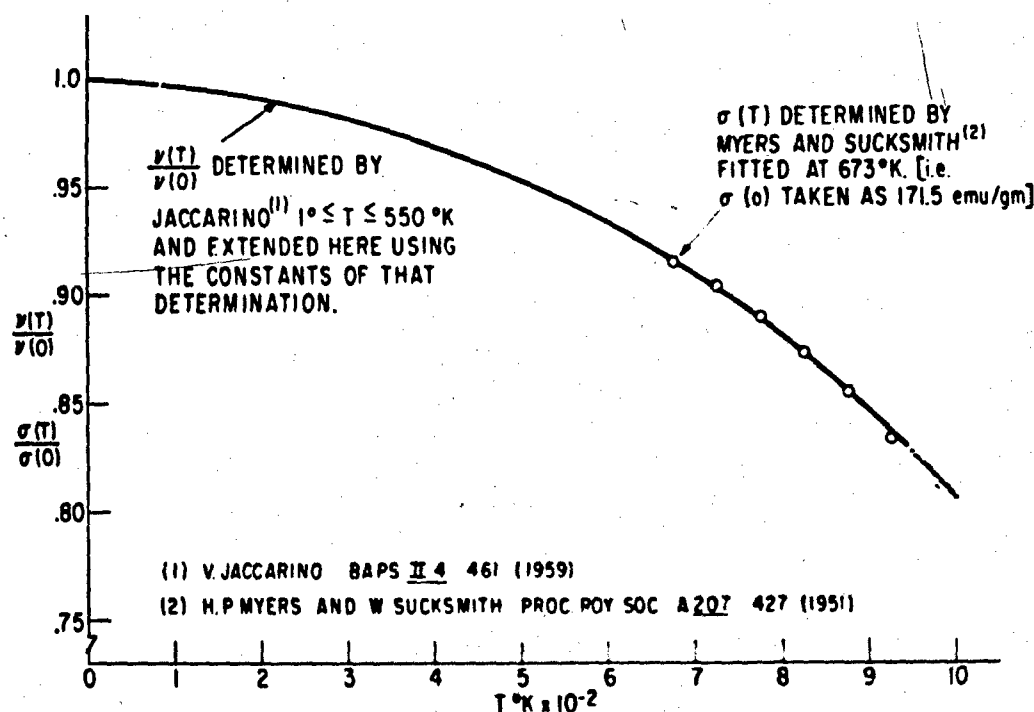
Fig. 7. The data of magnetization obtained by Myers and Sucksmith on bulk f.c.c. cobalt in the stable temperature range of that material compared with the nuclear resonance data of Jaccarino on fine powders of f.c.c. cobalt extrapolated to high temperatures.

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precipitate particles behavior is reasonably described by a power of nearly 20, the film samples give more nearly a 10th power behavior. Since we anticipated $p_2 \simeq 20$ the one type sample is well behaved while the other is anomalous. We do not understand this discrepancy.

Our primary result, i.e., K_1/M vs T is that the nuclear resonance frequency describes in f.c.c. cobalt a measure of the magnetization with a temperature independent coupling constant. We verify this in part by a comparison of the data of Myers and Sucksmith[39] to the extrapolated predictions of Jaccarino's measurements. Figure 7 gives the comparison graphically where the σ data are fitted at 673°K. The fit obtained is quite good to 900°K and further predicts $\sigma(0) = 171_{0.5}$ emu/g, an entirely reasonable estimate.

Conclusions

Face-centered cubic cobalt between 4.2° and 800°K (1) obeys a "10th power law" relating $K_1(T)$ to $\nu(T)$ suggesting that $\nu(T) \sim \sigma(T)$; furthermore, (2) since $\nu(T)$ maps onto $\sigma(T)$, this implies that the hyperfine coupling constant is not strongly temperature dependent. (3) The strain dependence, $(1/K_1)\partial K_1/\partial\omega$ has a temperature independent value of approximately 4, and (4) the splitting factor, g, is 2.06 ± 0.03, independent of temperature.

4. Pulsed Field Magnetization Measurements
    in Compounds

(During the final quarter of the contract term a very brief review paper was pre-
pared for presentation at the International Conference on High Magnetic Fields,
November 1-4, 1961, in Cambridge, Mass. The text of this paper is included in
the Conference Proceedings to be published in book form by Technology Press
at MIT.)

PULSED FIELD MAGNETIZATION MEASUREMENTS IN COMPOUNDS

Measurement of the magnetization curves of materials in pulsed fields
$(H \sim 200$ kOe) is readily accomplished by application of familiar pickup coil
methods.[19, 40] The sample is placed in the most spatially uniform region of the
available field, inside one of a pair of balanced and opposing pickup coils, whose
output is integrated and displayed on an oscilloscope against a field or time signal.

The limitations as compared with measurements in steady fields are of two
types. One is sensitivity and the other embraces the potential shortcomings mostly
discussed by Kapitza[41] which arise from magnetization heating and relaxation
phenomena (mainly in paramagnetics) and the heating and moments induced by eddy
currents in highly conductive samples. The limitation in sensitivity is not particu-
larly severe and poses an appropriate challenge to the experimenter. Constant
susceptibilities (volume) are easily measured to an uncertainty of $\pm 0.5 \times 10^{-4}$, and
improvement of this can be expected.

Among the advantages, it will be assumed that it is more economical to
produce fields of this magnitude in pulses rather than continuously. The speed of
the measurement and the continuous recording for both increasing and decreasing
fields are inherent conveniences. The latter feature makes possible the observation
of hysteretic phenomena. The placement of the sample in the spatially uniform field
region is particularly well suited for studying sharply nonlinear magnetization effects,
in contrast to techniques depending upon field inhomogeneity.

The magnetization behavior of materials in high fields can yield useful
information whether the material be paramagnetic, ferromagnetic, ferrimagnetic,
antiferromagnetic, or some combination of these.* A number of examples of the
application of pulsed field magnetization techniques to magnetic problems have

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*A table of published data on material having high field differential susceptibilities,
dM/dH, which are relatively constant over appreciable ranges of magnetic field
has been prepared by the author for American Institute of Physics Handbook.
Some copies are available upon request as GE Research Lab. Rept. No. 61-RL-2661
(Appendix A of this report).

appeared. A selected summary follows: In disordered alloys containing some manganese in a weakly magnetic or nonmagnetic host the observed failure to attain saturation provides support for a model of a spatially inhomogeneous ferro-antiferromagnetic state.[42] In a number of ferrimagnetic oxides[43, 44] questions regarding the value of the spontaneous moment and the presence of competing anti-ferromagnetic interactions leading to noncollinear spin configurations have been successfully attacked. The magnitude of such interactions is directly measured by the differential susceptibility at high fields, in favorable cases. In antiferro-magnetic materials a relatively abrupt increase in magnetization may indicate a spin-flopping process as observed in MnF_2[45] and in the ordered alloy Au_3Mn[46] providing a direct measure of the antiferromagnetic anisotropy. High fields have also induced transitions between states of different net magnetization which are connected by first order transformations in zero field as in the case of $MnAs$[47] at temperatures above its first order Curie point.

Another kind of measurement of interest depends not so much on the magnitude of the pulsed field but on its momentary nature, lying between steady field durations and the high frequencies employed for resonance techniques. That the pulsed field periods may span the relaxation times of certain rather slow magnetization processes may be viewed as an advantage instead of the contrary. As a consequence, increased hysteresis losses and two types of magnetic viscosity phenomena have been observed in certain ferrimagnetics.[48]

The examples given are not intended to exhaust all the possibilities but should serve to illustrate the wide variety of problems that can be attacked by pulsed field magnetization measurements. The versatility of this technique, combined with its economy, will undoubtedly make it standard solid-state laboratory procedure in the near future.

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5. Magnetic Exchange and Structure in the Lanthanum Manganite Perovskites

This investigation which applies the two techniques of high field magnetization and neutron diffraction is included in Group B of this Summary Report because it is nearly complete. The experimental portions have been executed and much of the analysis has been carried out. A full manuscript will be prepared shortly.

This system, of which the compound $LaMnO_3$ is an end point, has been of considerable experimental and theoretical interest. The La^{3+} ion may be replaced by ions such as Ca^{2+}, in which event some of the Mn^{3+} ions go over to Mn^{4+}. The general series formula is then $(La_{1-x}Ca_x) Mn^{3+}_{1-x} Mn^{4+}_x)O_3$. Such systems were first investigated by Jonker and van Santen[49] at the Philips Laboratories in Eindhoven, and they observed that at the end points $x = 0$ and $x = 1$ the compounds behaved as antiferromagnetic insulators, while at intermediate values of x, a considerable spontaneous magnetization developed and along with it, a significant conductivity. It was Zener,[50] in 1951, who first pointed out that electron or hole hopping between the Mn ions of different valence could give rise to a ferromagnetic exchange in competition with the antiferromagnetic superexchange, as well as providing a mechanism for the conduction. The process was termed "double exchange." It was investigated theoretically by Anderson and Hasegawa[51] and in an alternate way by Goodenough.[52] Neutron diffraction studies by Wollan and Koehler[53] on this system confirmed the general feature of antiferromagnetic- and ferromagnetic-like structures, but showed that intermediate cases were rather complex.

In the composition region of interest, that between 0 and 30 per cent Mn^{4+}, spanning the transition from antiferromagnetism to ferromagnetism, the compounds may also be prepared by introduction of cation vacancies through variations of heat treatment in different atmospheres. In this case, which applies to most of the samples examined herein, the typical formula may be written $LaMn^{3+}_{1-4x}Mn^{4+}_{3x}\square_xO_3$.

In the transition region the existing theoretical models are somewhat at variance with each other. Wollan and Koehler in their analysis of the neutron diffraction patterns in this region, including the effects of magnetic field on the observed reflections, conclude that the balance of evidence favors a description invoking a single crystallographic phase with an incoherent mixture of ferro- and antiferromagnetic regions or domains. Magnetically speaking, the transition compositions appeared to consist of two phases. A single magnetic phase did not seem compatible with their results in the framework of theoretical models current at the time. Such models are best categorized as single-magnetic axis structures, having all the magnetic spins parallel or antiparallel to a particular crystal axis. The concurrent analysis by Goodenough,[52] which capably accounts for many of the observations, also treats this transition range as a two-magnetic phase region. Although his analysis is expressed in terms of his theory of semicovalent bonding and exchange, it is equally well translated into the presently more popular crystal (ligand) field theory with the same conclusions.

By contrast, the re-examination of the effect of double exchange in magnetic crystals published last year by deGennes[54] allows a description of these compounds in terms of a single magnetic phase. It also seems capable of accounting for those observations which led Wollan and Koehler to favor the two-magnetic phase mixture. DeGennes showed that the competition between double exchange (ferro-) and super exchange (antiferro-) would tend to create a canted magnetic spin structure, whose angle of cant would vary linearly with the concentration of holes (or Mn^{4+} ions).

The deGennes model predicts a high field susceptibility, and such is observed in our experiments on compounds in this transition region (see Fig. 8). Of particular importance to a specific confirmation is the relation of these obser- vations to the different models described above. Each model is characterized by a definite relation between the spontaneous magnetization and the high field sus- ceptibility. Consider first the two-magnetic phase model. At vanishingly low Mn^{4+} concentration the susceptibility would be that of the antiferromagnetic "phase" and no spontaneous magnetization (meaning no ferromagnetic "phase") would be present. As the Mn^{4+} content builds up, the fractions of these two phases change, as measured, say, by the spontaneous magnetization. At some critical composition the whole sample is in the ferromagnetic phase. During the transition the high field antiferromagnetic susceptibility should decrease from its full value to keep up with the change in fractions of the two phases present. At the midpoint of the transition range, the susceptibility would have dropped to half of its value in the "pure" antiferromagnetic phase. If $M_0(x)$ is the spontaneous magnetization and $k(x)$
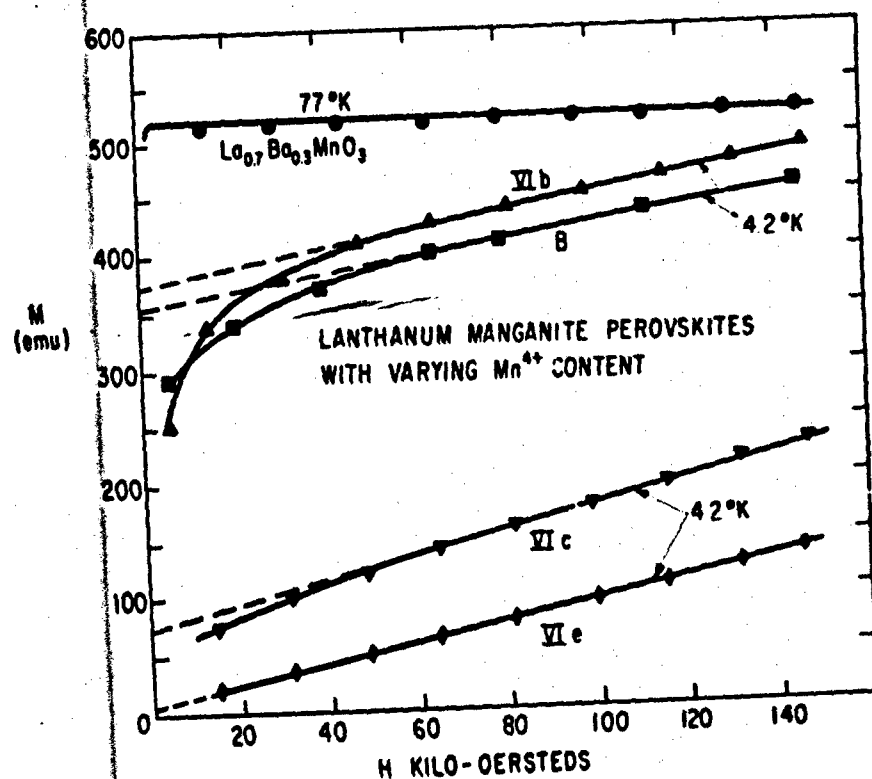
Fig. 8 Low-temperature magnetization curves for various lanthanum manganite perovskites.

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is the high field susceptibility at some Mn^{4+} content, and if $x = c$ designates the composition at which the full ferromagnetic contribution first occurs, then this model predicts very crudely for $0 \leq x \leq c$,

$$M_0 (x) = M_0 (c) x/c \qquad (4)$$

$$k (x) = k (0) (c - x)/c \qquad (5)$$

[In more detail, $M_0 (c)$ and $k (0)$ should be replaced by slowly varying functions of x].

The deGennes canted spin single-phase model predicts that the high field susceptibility would be roughly independent of composition in this transition range, i.e., instead of Eq. (5) one would have

$$k (x) = k (0) \qquad , \quad 0 \leq x < c \qquad . \qquad (6)$$

The results are listed in Table I and shown in Fig. 8. The compound with Ba^{2+} substitution was chosen to lie in the fully ferromagnetic range, and shows the essentially zero high field susceptibility expected of noncanted ferri- or ferromagnetic spin structure. It may be noted that the absence of a measurable high field susceptibility does not prove the absence of a canted spin structure, but, within the limits of the measuring sensitivity, it puts a lower limit on the exchange fields responsible for a possible canted structure. This question is tested further by recourse to other information, such as theoretical atomic models and experiments in neutron diffraction.

TABLE I

Low-temperature* Magnetization Data on Lanthanum Manganite Perovskites

Sample	%Mn^{4+} of Total Mn	M_0(emu)	$k \times 10^4$ cgs moment/ cc Oe	n_b (exp) / n_b (ferro-spin only)
$LaMnO_3$--VIe	0 ± 4	10	8.0 ± 0.5	0.02
$LaMnO_3$--VIc	5 ± 4	80	$10.5 \pm .5$	.13
$LaMnO_3$--B	18 ± 4	355	$7.5 \pm .5$	.63
$LaMnO_3$--VIb	9 ± 4	375	$8.0 \pm .5$	.65
$La_{0.7}Ba_{0.3}MnO_3$--III	~ 34	520	$< .5$	.92

*Measured at 4.2°K except the barium substituted sample for which T = 77°K.

The remaining four compounds show an approximately constant high field susceptibility, determined over the field range from 50 to 150 kOe. These cover a wide range of fractional spontaneous magnetization relative to the theoretical maximum (assuming spin only for the Mn^{3+} and Mn^{4+} ions). This fraction appears crudely as x/c in Eq. (4) and as n_b (exp)/n_b (ferro-spin only) in Table I, running from nearly zero up to 0.6. This behavior of the susceptibility is a clear consequence of the deGennes single-phase model and rules out a two-magnetic phase model. The valence distribution data (per cent Mn^{4+}) should be considered with due regard for the rough error limits. Such apparent inconsistencies have plagued other investigations in this system, but the consensus is that M_0 is approximately linear in Mn^{4+} content.

The high field susceptibility in the canted model should be approximately equal to the transverse susceptibility of the pure antiferromagnetic end point compound $LaMnO_3$. Such a comparison is difficult because most preparations deviate enough from stoichiometry to exhibit some spontaneous moment at low temperature. This effect of the double exchange will distort the low field susceptibility values both above and below the Néel point, as well as displacing both the Néel point and the paramagnetic Curie point. The "best" literature value for k appears to be 13.2×10^{-4}, which is higher than observed herein by about 50 per cent. Data are not available to estimate the reliability of this value.

An alternative estimate of this susceptibility value can be attempted by comparison with the behavior of other perovskite antiferromagnetics, such as $LaCrO_3$ or $LaFeO_3$. These last two differ from $LaMnO_3$ in their magnetic structure, having an alternating spin structure in which all nearest neighbor interactions are antiferromagnetic, and no others are needed to account for the observations.[55] $LaMnO_3$, however, has a layer structure in which in-plane superexchange interactions are ferromagnetic and out-of-plane superexchange is antiferromagnetic. The peculiarity of the $Mn^{3+} - O^{2-} - Mn^{3+}$ superexchange in which the sign is dependent upon direction has been discussed by Goodenough[52] and by Kanamori.[56] It is only the antiferromagnetic interaction that enters into the high field susceptibility.

We wish to calculate the susceptibility at the Néel point of a hypothetical $LaMnO_3$ having an alternating spin structure with only antiferromagnetic nearest neighbor interactions. The calculations and tabulations by Smart[55] are useful in this estimate. We use

$$k = C/(T + \theta) \quad , \quad T \geq T_N \tag{7}$$

be evaluated at $T = T_N$. For Mn^{3+} ions, with spin-only moment, C = 0.132 on a unit volume basis. We assume $T_N = 100°K$ as observed on real $LaMnO_3$, although this is certainly too high for the hypothetical structure, as it includes the ferromagnetic superexchange contribution.[11] The ratio θ/T_N for an alternating antiferromagnet with ions of spin 2 is calculated in the Bethe-Peierls-Weiss

approximation by Smart to be 1.25. The value observed for this ratio in $LaCrO_3$ is about 1.75. Using the theoretical estimate, the value of k (T_N) is about 6×10^{-4}, or about three-quarters of the measured high field susceptibility. Lowering the T_N assumed for the hypothetical compound to about 75°K would bring perfect agreement. In the spirit of this highly qualitative estimate, and the earlier cited experimental estimate, the observed value of k near 8×10^{-4} seems quite plausible.

While the neutron diffraction investigation on this system by Wollan and Koehler contributed greatly to the understanding of many of its aspects, the revised theoretical approach of deGennes suggests there might be some merit in a "second look" with neutrons. In earlier work, W. L. Roth had examined the neutron diffraction pattern of the compound $La_{0.7}Ba_{0.3}MnO_3$ and found good correspondence to a ferromagnetic spin structure. The same sample material has now been measured at high fields, as reported in Table I. We proposed to examine the neutron scattering from oxygen-rich $LaMnO_3$ to see whether evidence could be obtained for distinguishing between the "two magnetic phase" model and the "canted spin" model. Neutron diffraction patterns have been obtained at 295° and 4.2°K from sample $LaMnO_3$-B. Since the low-temperature spontaneous magnetization of this specimen was $M_0 = 355$ (emu) (approximately 60 per cent of the ferromagnetic spin value), it is roughly in the middle of the antiferromagnetic-ferromagnetic transition region of interest. The data have been only partially analyzed, and the preliminary results given here will be extended (and possibly modified) in the final manuscript.

The diffraction patterns were indexed with an orthorhombic unit cell based on the $GdFeO_3$ structure, space group D_{2h}^{16}-Pbmm, with a = b = 5.522 A and c = 7.740 A. The intensities of the strong peaks in the room temperature pattern agree reasonably well with those computed for nuclear scattering from an "ideal" perovskite arrangement, but since there are significant discrepancies between the observed and calculated intensities of the weaker peaks it is clear that the atomic structure is appreciably distorted from ideal. For this reason, it is not possible to subtract theoretical nuclear components from the low-temperature neutron diffraction pattern to obtain the scattering from the magnetic structure. The uncertainty in our knowledge of the precise atomic arrangement was obviated by constructing a difference pattern by point-by-point subtraction of the room temperature and low-temperature patterns. The difference pattern is due to the magnetic ordering if there is no change in atomic structure between 295° and 4.2°K.

The difference pattern showed five well-resolved peaks which could be measured with reasonable accuracy. Since no diffuse scattering or peak broadening was observed, only models based on long-range magnetic order were considered. A comparison of observed and calculated intensities for "canted spin" and "two magnetic phase" models is given in Table II. The intensity scale was set by normalizing with respect to the strong nuclear reflections.

The canted spin model gives excellent agreement with the observed magnetic scattering, and from the magnitudes of the intensities we deduce the cant angle (the angle between atomic spins in adjacent 001 planes) is 71°30' and the average magnetic moment per Mn site is $3.13\mu_B$.

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TABLE II

Difference Neutron Diffraction Pattern
$LaMnO_3$-B

Reflection Type	h k l	2θ	Canted Spin	Two Magnetic Phase I	II	Observed
				Neutron Intensity I(4.2°K) − I(295°K)		
Anti	001	7°26'	282	282	282	279
Ferro	110	14°52'	111	111	148	
Ferro	002	15°00'	$\underline{111}$	$\underline{111}$	$\underline{74}$	
			222	222	222	227
Anti	111	16°40'	103	103	103	116
Ferro	200 020	21°04'	43	43	58	
Ferro	112	21°12'	$\underline{129}$	$\underline{129}$	$\underline{114}$	
			172	172	172	168
Anti	201 021	21°04'	41	41	41	
Anti	003	21°12'	$\underline{18}$	$\underline{18}$	$\underline{18}$	
			59	59	59	53

     Equally good agreement is obtained with the two-phase model. Calculations were carried out for two different two-phase models. In (I), the antiferromagnetic phase is the (001) layer structure observed by Wollan and Koehler[53] for pure $LaMnO_3$, and in the ferromagnetic phase the moments are randomly distributed among <100> directions. In (II), the moments in the ferromagnetic phases are collinear with those in the antiferromagnetic phase. The neutron diffraction difference pattern is quantitatively satisfied by the two-phase model with 66 per cent ferromagnetic phase and an average moment of $3.13\mu_B$.

     Thus at the present stage of analysis the neutron diffraction on powders of this material does not distinguish between the two models, i.e., the two magnetic phase model and the canted spin model. At the same time the evidence from the magnetization measurements does distinguish them, in favor of the deGennes[54] canted spin model. Prior to final recording certain reconciliations are needed to bring together slightly differing numbers deduced from the two independent experimental methods employed.

GROUP C

1. On the Existence of an Intermediate Antiferromagnetic State
    in Hausmannite and Isomorphous Mixed Manganites

Preliminary exploratory experiments were undertaken early in the contract
term to investigate the nature of the magnetic state existing at temperatures above
the ferrimagnetic Curie point of Mn_3O_4 ($T_C = 42°K$) and isomorphous compounds
containing partial substitution of diamagnetic Zn^{2+} or Mg^{2+} ions for Mn^{2+} in the
tetrahedral sites of Mn_3O_4. These compounds have figured in recent studies prior
to this contract by Jacobs[43] and by Jacobs and Kouvel.[48]

The first of these studies showed that these compounds, in powder form,
exhibit a constant differential magnetic susceptibility at high magnetic fields and
low temperatures superposed on their spontaneous ferrimagnetic moment. This
was interpreted as evidence for the existence of triangular or canted ferrimagnetic
arrays predicted in 1952 by Yafet and Kittel.[57] These arrays may be expected
when the intra-site interaction (e.g., antiferromagnetism within the octahedral
sites of the spinel-like structure) is comparable to the inter-site interaction (e.g.,
antiferromagnetic coupling between the octahedral site ions and the tetrahedral
site ions). This conclusion was substantiated by the neutron diffraction work of
Kasper[58] on Mn_3O_4.

The second of the above-named studies showed that the manganites with
partial diamagnetic substitutions exhibit a unidirectional anisotropy (displaced
magnetic hysteresis loop) when cooled in magnetic fields of several kOe. To
account for this, an exchange anisotropy model was proposed that involved inter-
actions between ferrimagnetic and nearly antiferromagnetic regions brought about
by the random distribution of the diamagnetic ions among the tetrahedral sites and
the consequent magnetic inhomogeneity. Some support for this model rests on the
evidence that the fully substituted $ZnMn_2O_4$ and $MgMn_2O_4$ are probably antiferro-
magnetic. However, difficulties arose in accounting for the nucleation of the
requisite preferred magnetic orientations as well as for the persistence of the
unidirectional anisotropy up to the ferrimagnetic Curie point. It appeared possible
to resolve these difficulties if the phenomena leading to the unidirectional anisotropy
had their origin above the Curie point temperature.

The possibility of a partly antiferromagnetic state existing above a
triangular one had been foreseen by Yafet and Kittel and by Lotgering.[59] Indeed,
their theoretical model demanded that such be the case if the triangular state
persisted up to the ferrimagnetic Curie point. While the details of their model
have been subjected to criticism recently by Kaplan,[60] it is believed that this
feature will be preserved. However, there has been little or no evidence published
in support of the existence of such states.

In view of the foregoing, several experiments were designed to test for the existence of a cooperative magnetic state above the Curie points: Mn_3O_4, $T_C = 42°K$; $Zn_{0.3}Mn_{2.7}O_4$, $T_C = 31°K$; $Zn_{0.5}Mn_{2.5}O_4$ (or $Mg_{0.5}$), $T_C = 20°K$. The samples were cooled from room temperature to 77°K in steady magnetic fields of a few kOe. At this temperature they behaved "paramagnetically" in that there was no remanence observable, within the accuracy of the detector employed, and the moment induced was proportional to the field. The field was then removed and the samples were cooled to 4.2°K in a region in which the component of the earth's field along the axis of measurement had been reduced to less than 0.02 Oe. The remanence of the sample at 4.2°K was measured and it was found that a small value (several emu) was present dependent upon the sign and possibly on the magnitude of the field present during cooling to 77°K. This remanence (at 4.2°K) did not decay significantly with long retention of the sample at 77°K, nor could it be reversed in sign by modest fields applied at 77°K including fields up to twice those which originally created the state during cooling from room temperature to 77°K.

The phenomenon was observed on powders of the compounds for which Curie points are listed above, including Mn_3O_4 containing no diamagnetic substitution. The effect appeared to be present also in a natural crystal of Mn_3O_4 and in a polycrystalline boule, but the magnitude of the effect was considerably reduced in the crystal under that obtained in the powder.

Support for these ideas is found in a recent paper presented at the 1960 Magnetism Conference by V. L. Morruzzi[40] of the IBM Research Center. He reports torque measurements on an Mn_3O_4 crystal at 77°K with the axis of rotation perpendicular to the c-axis. The torque is proportional to H^2 and vanishes near 108°K. These results are consistent with the existence of the antiferro-magnetic state but also allow alternative interpretation.

These preliminary results suggest the presence of a cooperative stable magnetic state in the temperature range above the Curie points of these compounds. Further experiments are planned to substantiate or disprove the hypothesis, and to evaluate its significance. Background on a related problem in two-phase material is contained in a recent paper by Jacobs and Lawrence.[61]

2. The Interaction of Ultrasonic Waves
   with Ferromagnetic Bodies

Recent advances in the generation of ultrasonic waves with frequencies exceeding 10,000 Mc/s have opened an area of research concerning the interaction of such "phonons" with matter. One such area involves the interaction of these phonons with ferromagnetic bodies. The fact that this Laboratory (E. H. Jacobsen, in particular) has a pioneering lead in the field of microwave ultrasonic generation has allowed rapid and convenient access to experiments with ultrasound. Prior to this Contract and continuing as part of this Contract, we have examined interactions

between ultrasonic waves and magnetic bodies. A recent and encouraging result is that a thin film of nickel evaporated onto the end of a quartz rod has allowed us to change the attenuation of ultrasonic waves by application of an external d-c magnetic field in the plane of the film. These experiments are still in a preliminary state and are as yet neither fully understood nor exploited.

3. Magnetic Interactions and Spin Arrangements in Heavily Substituted Yttrium Iron Garnets

Exploratory high field experiments were carried out during the contract term on several powder samples of heavily substituted garnets, made available through the cooperation of Dr. S. Geller of the Bell Telephone Laboratories. The following formula unit is convenient to use:

$$\{Y_{3-y-z}Me_{y+z}\}\ [Fe_{2-y}M_y]\ (Fe_{3-z}M_z)\ O_{12} \quad .$$

The braces { } indicate ions in the dodecahedral sites or c-sites, the brackets [ ] refer to ions in the octahedral or a-sites, and the parentheses ( ) designate ions in the tetrahedral or d-sites. The valence state of the Fe ions is Fe^{3+}. If M is a quadrivalent ion, such as Si^{4+}, Sn^{4+}, or Zr^{4+}, Me is a divalent ion such as Ca^{2+}; if M is trivalent, so also is Me, which is then Y^{3+} or a rare-earth ion. A survey of such substitutions is presented in the paper by Geller, [62] resting mainly on the extensive work at BTL and at Grenoble.

The compositions under study are $\{Y_{1.5}Ca_{1.5}\}[Fe_{0.5}Sn_{1.5}]\ (Fe_3)\ O_{12}$ and $\{Y_{1.6}Ca_{1.4}\}\ [Fe_{0.6}Zr_{1.4}]\ (Fe_3)\ O_{12}$. The ionic distribution is well established from the careful x-ray work of Geller and associates. The spontaneous magnetization is less definitely fixed by the previous measurements to 12 kOe. The course of the spontaneous magnetization at low temperature as a function of Sn or Zr substitution is the subject of two different theoretical approaches. One by deGennes[63] uses a molecular field approach along the lines of the Yafet-Kittel-Lotgering theory of triangular or canted ferrimagnets. The alternate approach by Gilleo[64] is based on a statistical theory of randomly incomplete superexchange linkage brought about by the introduction of the nonmagnetic Sn or Zr ions. Measurements in higher fields are expected to fix the question of the spontaneous magnetization and to help distinguish between the theories by comparison with their predictions for high field susceptibility. Initial results appear to disagree with deGennes' theory.

4. The Anisotropy of Nickel Single-Crystal Films

We have grown by vapor deposition onto MgO substrates {100 } and { 111} plane single crystals of nickel and have measured by ferromagnetic resonance the temperature dependence of the anisotropy constants K_1, K_2. In attempting to fit the temperature dependence of the nuclear resonance data of nickel to the temperature

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depencence of K_1 we have used the nuclear resonance data of J.I. Budnick.* We are unable to obtain agreement with as simple a power law as in the case of cobalt. We find K_1 to be negative over the entire temperature range observed (to 600°K) contrary to the findings of Puzei[65] that indicate K_1 changes sign near 500°K.

5. Magnetocrystalline Anisotropy of the Rare-Earth Metal Gadolinium

We have succeeded in growing large single crystals of the rare-earth metal gadolinium. The rare earths offer a unique set of properties--many of these have not been studied in detail because of lack of good single crystals. We intend to measure the magnetocrystalline anisotropy as a function of temperature as well as the more detailed spin resonance behavior of gadolinium single crystals as a preliminary step to a more thorough understanding of other magnetic properties of the rare metals.

The single crystals of gadolinium have been oriented and machined for subsequent detailed measurements. We find it necessary to etch the surface deeply to remove machining strains--an etch that appears satisfactory for this purpose is a 50-50 mixture of methyl alcohol and nitric acid (this should be handled with care as it is also a rocket fuel). Following the etch, the samples are electropolished and given a final x-ray check to determine if excessive residual strain exists--this is estimated by the sharpness of the Laue spots.

A preliminary measurement of anisotropy by magnetic resonance method has yielded a definite result. We have established that the easy axis of the magnetization at room temperature is along the c-axis of the hexagonal structure, but that this changes to near the basal plane at liquid nitrogen temperature (77°K) and below that temperature may become very large in magnitude.

6. Nuclear Resonance in FeRh

Iron-rhodium alloys exhibit interesting magnetic properties. The alloy of near 50-50 composition is antiferromagnetic at room temperature but becomes ferromagnetic at temperatures exceeding 80°C. The interesting point and the feature of the system that we are concerned with here is that in the ferromagnetic state if one assigns a moment of $2.2\mu_b$/iron atom (as is usual) then the recent experimental work of Kouvel et al. at this Laboratory would require the rhodium atoms to each carry magnetic moments of $1.5\mu_b$. Since Rh^{103} is a 100 per cent naturally abundant isotope of spin 1/2 and known nuclear moment, the observation of its nuclear resonance frequency would allow estimation of the hyperfine field at the Rh nucleus in the ferromagnetic state of the FeRh alloy and subsequently a reasonable estimate of electronic magnetic moment on each rhodium atom. Since

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*Private communication.

rhodium metal is not ferromagnetic nor do the rhodium atoms in it carry a large unbalanced moment, the problem of FeRh is of particular interest and we have been searching for the nuclear resonance in that system, so far without success.

7. Antiferromagnetic Behavior of $FeCO_3$

A study of $FeCO_3$ was undertaken during the latter part of the contract term in the hope of discovering a spin-flop transition as in MnF_2 (cf. Group B, Section 2) or a metamagnetic transition from antiferromagnetism to ferromagnetism. Such a transition, when properly identified and analyzed, enables one to specify the anisotropy characteristic of this compound. Previous work on $FeCO_3$ is as follows: Foex[66] investigated the highly anisotropic susceptibility in the paramagnetic range on a natural mineral crystal (siderite); Becquerel[67] studied the Faraday rotation above and below the magnetic ordering temperature on two mineral samples, suggesting ordering temperatures near $60°K$ for one and near $35°K$ for the other; Bizette[68] studied the susceptibility as a function of temperature down to $14°K$ on a natural crystal with a Néel temperature near $35°K$ and on synthesized powder with a Néel temperature near $57°K$; Alikhanov[69] recently examined the magnetic structure by neutron diffraction on a mineral sample finding a Néel point at $35°K$, with the atomic moments aligned antiferromagnetically parallel to the c-axis (trigonal symmetry) of the rhombohedral calcite structure. From the specific results obtained in neutron diffraction, as well as from inferences following the works of Becquerel and Bizette, one would identify $FeCO_3$ as a likely choice for the occurrence of an abrupt magnetic transition, in contrast to $MnCO_3$ and $CoCO_3$ whose magnetic moments lie antiparallel, in the basal plane of the calcite structure.

The initial work has been done on powder and nearly monocrystalline specimens obtained from natural siderite samples found at Roxbury, Connecticut, and purchased through Ward's Natural Science Establishment, Rochester, New York. Chemical analysis and x-ray diffraction have revealed a second phase impurity (about 6 per cent by weight) in the form of SiO_2 (quartz), and some solid solution impurities of $MnCO_3$ and alkaline earth carbonates (Ni, Co, and Zn were not detected). An approximate formula is $(Fe_{0.84}Mn_{0.05}A_{0.11})CO_3$, where A is Mg and/or Ca, Sr, or Ba.

Magnetization measurements on a nearly monocrystalline sample, in fields up to 140 kOe, at $4.2°K$, with H along the trigonal axis, have revealed the start of a rather sharp magnetic transition near 100 kOe. It was initially surmised to be a spin-flop, but theoretical considerations by Kanamori[70] pertaining to $FeCl_2$ raise the strong possibility that this will be a metamagnetic transition to a ferromagnetic state as observed in $FeCl_2$. This question will be experimentally resolved by extending the measurements to about 180 kOe.

Susceptibility measurements as a function of temperature on powder from the same source, carried out with the cooperation of J.S. Kouvel and C.C. Hartelius, reveal a peak in the susceptibility near $39°K$, and also show, in agreement with

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Bizette, that the ratio of the powder susceptibility at the peak to that at low temperature is 3 or 4 to 1. The possibility of preferred orientation in pressing the powder into a sample pellet is being studied. Ratios as high as this are outside the usual framework of the molecular field theory pertaining to a simple uniaxial antiferromagnet, and are rarely found. The compound $FeCl_2$ is another example of this, and prompted the above-mentioned analysis by Kanamori which may prove to be highly applicable to $FeCO_3$. Compounds of this class are characterized by highly anisotropic exchange, approaching the extreme represented by the Ising model in which moments are restricted to have components only along a single axis. The recent theoretical treatment of Fisher[71] would apply here, with the interesting possibility, as shown in his model, that the magnetic ordering temperature lies below the peak susceptibility.

An additional observation of interest by Kouvel and Hartelius on this siderite powder, is that a small remanent magnetization amounting to 0.1 emu/g of sample appears at 4.2°K upon cooling the sample to that temperature from 80°K in a field of 5000 Oe. This remanence is unaffected by a reverse field of 10 kOe, producing an asymmetric loop. A possible explanation for this is to ascribe the moment to imperfect compensation owing to the Mn impurity ions having a different moment from the Fe ions. These appear to be rigidly bound to the $FeCO_3$ antiferromagnetic array, and hence remain oriented after the field cooling until fields are reached which disrupt the $FeCO_3$ magnetic array. Several other hypotheses are tenable, but this seems simplest.

Further work is planned on samples of higher purity, if available, and measurements to higher magnetic fields both on powder and monocrystalline forms.

SUMMARY

This Final Report describes a number of research projects dealing with fundamental interactions and the microstructure of internal fields in selected magnetic materials were carried out. (a) The nuclear magnetic resonance of Co^{59} in metallic cobalt powders has been examined. In addition to the absorption characteristic of Co^{59} in face-centered cubic cobalt, there were found an additional group of absorptions, one of which is clearly associated with hexagonal close packed cobalt. (b) The phenomenon of spin-flopping in antiferromagnetic MnF_2, in which the axis of antiferromagnetism is decoupled from the crystal axes, was observed by magnetization measurements in high pulsed magnetic fields. Its position coincided with the value, 93 kOe, predicted from measurements of antiferromagnetic resonance with millimeter microwaves. (c) The temperature dependence of the magnetocrystalline anisotropy of face-centered cubic cobalt metal was examined by ferromagnetic resonance on single crystal thin films and submicron precipitate particles in Cu, at temperatures below the range in which this is the stable structure. Satisfactory agreement is obtained for a tenth power law between anisotropy and magnetization. (d) A very brief review paper on pulsed field magnetization measurements in compounds was prepared. (e) An investigation of magnetic

exchange and structure in lanthanum manganite perovskite compounds spanning the transition between antiferromagnetism and ferromagnetism was performed using neutron diffraction and high field magnetization techniques. Evidence favored the single-phase canted spin model for this region over the model of a mixture of two crystallographically similar but magnetically distinct phases. (f) Seven additional exploratory projects were undertaken, some of which hold considerable promise for development. In particular, immediate plans for future work are concentrated on the investigation of the ferromagnetic resonance study of the rare-earth metal gadolinium and the investigation of the antiferromagnetic behavior of $FeCO_3$.

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MAGNETIZATION BEHAVIOR IN HIGH MAGNETIC FIELDS

I. S. Jacobs

The magnetization behavior of materials in high magnetic fields (H > 25 kOe) can yield useful information whether the material is paramagnetic, ferromagnetic, ferrimagnetic, antiferromagnetic, or some combination of these. Typically interesting results include comparison with a Langevin-Brillouin curve, reflecting the energy level structure in paramagnetics; the value of the saturation moment, including paramagnetic saturation; failure to achieve saturation owing to large anisotropies or to nonferromagnetic interactions; the value of the spontaneous moment, and the presence or absence of a differential susceptibility at high fields characterizing a nonferromagnetic interaction; and relatively abrupt changes in magnetization indicating antiferromagnetic spin-flopping, metamagnetic behavior, or first-order transformations. Table A-1 presents data from materials having differential susceptibilities, dM/dH, which are relatively constant over appreciable ranges of magnetic field. It excludes high field data which indicate only linear extrapolation of low field susceptibility measurements. Thus, the low field behavior of the substances tabulated is either hysteretic, nonlinear, or the precursor of a differential susceptibility of rather different magnitude. For details of the large amount of high field magnetization research, pertaining to much of the behavior listed above but outside the scope of this table, reference should be made to the original papers, largely by the same authors whose work is tabulated herein.

TABLE A-1

Magnetic Susceptibilities in High Fields--
$$\chi_V = \kappa = dM/dH \text{ cgs Moment/cm}^3 \text{ Oersted}$$

Substance	Form*	Temp (°K)	H Range (kOe)	Vol. Susc. $(10^4 \kappa)$	Ref.
Ni	P	288	50-290	0±0.2	1
Fe	P	288	50-260	0±0.7	1
Fe	P	1.3-4.2	10- 60	0±0.8	2
Gd	P	1.3-4.2	10- 60	0±0.8	4
18-8 Stainless steel	P	288	50-260	0.4±0.02	1
γ-Fe_2O_3	P	4.2	20- 60	0±0.2	3
Fe_3O_4	P	4.2	20-140	0±0.5	5
Mn_3O_4	P	4.2	60-140	3.0±0.5	5
Mn_3O_4	C(a)	4.2	15- 75	3.5±0.5	7

Table A-1 (continued)

Substance	Form*	Temp (°K)	H Range (kOe)	Vol. Susc. ($10^4 \kappa$)	Ref.
$Zn_t Mn_{2-t} O_4$					
t = 0.3	P	4.2	60-140	3.5±0.5	5
t = 0.5	P	4.2	60-140	2.6±0.5	5
t = 0.93	P	4.2	20-140	2.3±0.5	5
$Mg_{0.5}Mn_{2.5}O_4$	P	4.2	40-140	3.2±0.6	5
$Mg\ Mn_2O_4$	P	4.2	40-140	2.7±0.5	5
$Co_t\ Mn_{2-t}\ O_4$					
t = 0.5	P	4.2	60-140	3.0±0.5	5
t = 0.75	P	4.2	60-140	3.0±0.5	5
t = 0.92	P	4.2	60-140	3.6±0.5	5
$Mn\ Fe_2O_4$	P	77	10-140	0±0.5	6
$Mn\ Fe_2O_4$	C	4.2	5- 75	0.7±0.5	7
$Mn\ Cr_t Fe_{2-t}O_4$					
t = 0.5	P	4.2-77	10-140	1.0±0.7	6
t = 1.0	P	4.2-77	20-140	2.7±0.7	6
t = 1.5	P	4.2-20	20-140	3.4±0.5	6
$Mn\ Cr_2O_4$	P	4.2	20-140	3.6±0.5	6
$Mn_t\ Fe_{3-t}O_4$					
t = 1.25	C	4.2	5- 75	1.4±0.5	7
t = 1.55	C	4.2	5- 75	1.7±0.5	7
t = 1.80	C	4.2	5- 75	2.3±0.5	7
$CuCr_2O_4$	P	4.2	80-140	1.3±0.5	6
$Fe\ Cr_2O_4$	P	4.2	50-140	3.9±0.5	6
$Ni\ Cr_t\ Fe_{2-t}O_4$					
t = 0.5	P	4.2	20-140	0±0.5	6
t = 1.0	P	4.2	10-140	0±0.5	6
t = 1.5	P	4.2	60-140	3.0±0.5	6
t = 1.85	P	4.2	~80-140	~1.0	6

Table A-1 (continued)

Substance	Form*	Temp (°K)	H Range (kOe)	Vol. Susc. $(10^4 \kappa)$	Ref.
Ni Cr_2O_4	P	4.2	60-140	~1.0	6
Zn Fe_2O_4†	P	4.2	10-140	18.0±0.5	9
Mn F_2**	C(c)	4.2	0- 70	0±0.5	8
Mn F_2**	C(c)	4.2	110-150	10.3±0.5	8
Mn F_2**	P	4.2	0- 30	6.9±0.5	8
Mn F_2**	P	4.2	110-150	10.3±0.5	8
Mn Au_3 (ord.)‡	P	4.2-77	0- 10	11.3±0.3	10
Mn Au_3 (ord.)‡	P	4.2-77	70-140	24.0±0.5	10
Cr O_2	P	4.2	20-140	0±0.5	9

FOOTNOTES AND REFERENCES FOR TABLE A-1

Footnotes:

*P = powder or polycrystalline solid.

C = single crystal.
   (a) = basal plane
   (c) = c- axis

†Ionic distribution nearly normal.

**Spin-flop H_c = 93 ± 2 kOe.

‡Spin-flop H_c = 47 kOe.

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APPENDIX B

ANALYSIS OF RESONANCE DATA

THE GENERAL RESONANCE CONDITION

If we can describe the orientation dependent energy of a system (in this case a magnetic system) by $E = E(\theta, \phi)$ where θ, ϕ, are the polar and azimuthal angles of the magnetization, M, with respect to a coordinate system, then at equilibrium the net torque is zero, i.e., $\partial E/\partial \theta = \partial E/\partial \phi = 0$, and determines the equilibrium orientation of M to be (θ_0, ϕ_0). The energy E contains all spatially dependent terms including shape (demagnetizing), applied field, and magneto-crystalline anisotropy. We examine the restoring torques (i.e., the stiffness) of the system (assumed fully magnetized) by expanding the energy into a Taylor series about (θ_0, ϕ_0) and determine the resonant frequency to be given by

$$\omega = \frac{\gamma}{M \sin \theta} \left[\frac{\partial^2 E}{\partial \theta^2} \cdot \frac{\partial^2 E}{\partial \phi^2} - \left(\frac{\partial^2 E}{\partial \theta \partial \phi} \right)^2 \right]^{1/2} , \tag{B1}$$

a result first described by Suhl.[1] γ is the magnetomechanical ratio.

For a spherical sample having cubic magnetocrystalline anisotropy constants K_1, K_2, and in the approximation that $H \gg K/M$ with the applied field H in a {110} crystallographic plane and θ measuring the angle from a <100> crystallographic direction we find from (B1) the expression

$$\frac{\omega}{\gamma} = H + \frac{1}{2M} \left[K_1 \left(-\frac{3}{8} + \frac{5}{2} \cos 2\theta + \frac{15}{8} \cos 4\theta \right) + \right.$$

$$\left. K_2 \left(-\frac{7}{32} + \frac{5}{64} \cos 2\theta + \frac{15}{32} \cos 4\theta - \frac{21}{64} \cos 6\theta \right) \right] \tag{B2}$$

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With the field along a principal direction, i.e., one along which E has an extremum, the magnetization will align with the field and the results from (B2) are that for

$$H \parallel \langle 100 \rangle; \quad \frac{\omega}{\gamma} = H_{100} + \frac{2K_1}{M} \tag{B3a}$$

$$H \parallel \langle 110 \rangle; \quad \frac{\omega}{\gamma} = H_{110} - \frac{K_1}{2M} + \frac{K_2}{4M} \tag{B3b}$$

$$H \parallel \langle 111 \rangle; \quad \frac{\omega}{\gamma} = H_{111} - \frac{4}{3}\frac{K_1}{M} - \frac{4}{9}\frac{K_2}{M} \tag{B3c}$$

If the field is not along a direction of an energy extremum, then the magnetization will not precisely align with the field and one must calculate the misalignment; Artman[2] has given a helpful treatment of this problem. For example with the field H|| $\langle 211 \rangle$ and assuming M || H

$$\frac{\omega}{\gamma} = H_{211} - 0.5 \frac{K_1}{M} - 0.1389 \frac{K_2}{M} \tag{B4}$$

It is clear, however, that M is not parallel to H except in limit K→0 or H→∞, and in fact as an example the condition for H ∦ $\langle 211 \rangle$ and a departure of $2°30'$ of M from H* gives (to first order in the deviation)

$$\frac{\omega}{\gamma} = H_{211} - 0.695_7 \frac{K_1}{M} - 0.1918_8 \frac{K_2}{M} \tag{B4'}$$

The correction required in any particular case depends on the size of K/MH and is therefore temperature dependent. The calculation is important in properly analyzing the K_2/M anisotropy determination for the Co-precipitate particles of the (111) plane oriented sample.

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2. J. O. Artman, Proc. I.R.E., **44**, 1284 (1956).

* The departure will be toward lower energy positions which for K_1 negative is toward the nearest $\langle 111 \rangle$.

The situation for a thin film sample is considerably different because of the large shape anisotropy. In fact, the celebrated "Kittel condition"

$$\frac{\omega}{\gamma} = [H(H + 4\pi M)]^{1/2} \tag{B5}$$

describes the condition for resonance in an isotropic (no crystal anisotropy) thin film with the field H in the plane of the film. With cubic crystal anisotropy and a thin film having a (100) crystallographic plane coplanar with the plane of the film we find

$$H \parallel <100> \frac{\omega}{\gamma} = \left\{ \left[H_{100} + \frac{2K_1}{M} + 4\pi M \right] \left[H_{100} + \frac{2K_1}{M} \right] \right\}^{1/2} \tag{B6a}$$

$$H \parallel <110> \frac{\omega}{\gamma} = \left\{ \left[H_{110} + \frac{K_1}{M} + \frac{1}{2}\frac{K_2}{M} + 4\pi M \right] \left[H_{110} - \frac{2K_1}{M} \right] \right\}^{1/2} \tag{B6b}$$

If the plane of the film is a (111) crystallographic plane we find

$$H \parallel <110> \frac{\omega}{\gamma} = \left\{ \left[H_{110} - \frac{K_1}{M} - \frac{K_2}{6M} + 4\pi M \right] \left[H_{110} + \frac{K_2}{3M} \right] \right\}^{1/2} \tag{B7a}$$

$$H \parallel <112> \frac{\omega}{\gamma} = \left\{ \left[H_{112} - \frac{K_1}{M} + \frac{9.45}{64}\frac{K_2}{M} + 4\pi M \right] \left[H_{112} - \frac{K_2}{3M} \right] \right\}^{1/2} \tag{B7b}$$

Because of the film geometry the magnetization never departs appreciably from the plane of the film (i.e., the demagnetizing factor $4\pi M$ is the principal constraint) and in the (111) plane the <112> is essentially an energy extremum. This situation removes the correction that was necessary in the case of the spherical precipitate particles.

The expressions given above are used as primary tools to obtain from the applied field required for resonance and the known microwave frequency the parameters K_1/M, K_2/M, and the spectroscopic splitting factor, g, contained in γ.