GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

Date: May 13, 1968

Project Title: Magnetic Phenomena at Metal Surfaces

Project No.: A-1024-001

Project Director: Dr. Stephen Spooner

Sponsor: United States Atomic Energy Commission

Effective April 1, 1968 Estimated to run until: March 31, 1969

Type Agreement: Mod. No. 1 to Contract AT-(40-1)-3674 Amount: $ 38,346*

Reports: Progress Report - due June 30, 1968
Final Report

Contact Person: U. S. Atomic Energy Commission
Oak Ridge, Tennessee 37830
Attn: Mr. Ralph Elson, Director
Contract Division
Oak Ridge Operation

*plus $5,477 to be transferred from A-1024 budget and $12,783 as Ga. Tech's contribution to meet cost-sharing requirements, for a total of $56,606 available to the project. A division "E" Account must be established early in FY 69 fro charging the Ga. Tech portion of costs.

Assigned to Physical Sciences Division

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GEORGIA INSTITUTE OF TECHNOLOGY
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PROJECT TERMINATION

Date June 18, 1969

PROJECT TITLE: Magnetic Phenomena at Metal Surfaces

PROJECT NO: A-1024-001

PROJECT DIRECTOR: Dr. Stephen Spooner

SPONSOR: United States Atomic Energy Commission

TERMINATION EFFECTIVE: March 31, 1969

CHARGES SHOULD CLEAR ACCOUNTING BY: All charges not encumbered or actually incurred prior to March 31, 1969 are not allowable.

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PROJECT INITIATION

Date: June 19, 1969

Project Title: Magnetic Phenomena at Metal Surfaces - III

Project No.: A-1024-002

Project Director: Dr. Stephen Spooner

Sponsor: United States Atomic Energy Commission

Effective . . . . . April 1, 1969 . . . . . Estimated to run until: . . . March 31, 1970 . . . . . .

Type Agreement: . Mod. No. 2 to Contract AT-(40-1)-3674 . . . . . Amount: $. 45,000* . . . . . .

Reports: Progress Report - due about December 31, 1969
Final Report

Contact Person: U. S. Atomic Energy Commission
Oak Ridge, Tennessee 37830

Attention: Mr. Ralph Elson, Director
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*Plus Ga. Tech contribution of $11,246; Companion Account No. E-700-200

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT TERMINATION

Date August 7, 1970

PROJECT TITLE: Magnetic Phenomena at Metal Surfaces - III

PROJECT NO: A-1024-002

PROJECT DIRECTOR: Dr. Stephen Spooner

SPONSOR: United States Atomic Energy Commission

TERMINATION EFFECTIVE: March 31, 1970

CHARGES SHOULD CLEAR ACCOUNTING BY: All charges have cleared.

Note: As of June 30, 1970, project shows $7,898.69 overrun including $832.00 encumbrance. Encumbrances should be removed and overrun transferred out.

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT INITIATION

Date: May 11, 1970

Project Title: Magnetic Phenomena at Metal Surfaces - IV

Project No.: A-1024-003

Project Director: Dr. Steven Spooner

Sponsor: U. S. Atomic Energy Commission

Effective April 1, 1970 Estimated to run until: March 31, 1971

Type Agreement: Mod. No. 3 to Contract No. AT-(40-1)-3674 Amount: $ 43,234*

Reports: Progress Report - due about December 31, 1970
Final Report

Contact Person: U. S. Atomic Energy Commission
Oak Ridge, Tennessee 37830

ATTENTION: Mr. Ralph Elson, Director
Contract Division
Oak Ridge Operations

*Plus GIT contribution of $10,180; Companion Account E-700-200.

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PROJECT TERMINATION

Date 4/7/71

PROJECT TITLE: Magnetic Phenomena at Metal Surfaces

PROJECT NO: A-1024-003

PROJECT DIRECTOR: Dr. Stephen Spooner

SPONSOR: Atomic Energy Commission

TERMINATION EFFECTIVE: 3/31/71

CHARGES SHOULD CLEAR ACCOUNTING BY: 4/30/71

Contractual Obligations Remaining:

1. Certified Expenditure Statement (Appendix "C") due by 6/30/71 (EES Accounting).

2. Report of Equipment Purchased or Fabricated - due by 6/30/71 (Dr. Spooner).

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PROJECT INITIATION

Date: 4/7/71

Project Title: Magnetic Phenomena at Metal Surfaces

Project No.: A-1024-004

Project Director: Dr. Stephen Spooner

Sponsor: Atomic Energy Commission

Effective April 1, 1971 Estimated to run until: March 31, 1973

Type Agreement: Mod. No. 4 to Contract No. AT-(40-1)-3674 Amount: $ 80,795.00*

*Plus Ga. Tech Contribution of $20,199.00;
Companion Account E-700-200.

Reports: Progress Report - due December 31, 1972.
Final Report - due March 31, 1973.

Contact Person: Mr. Earl Mason or Dr. Dent C. Davis
U. S. Atomic Energy Commission
Oak Ridge Operations
P. O. Box E
Oak Ridge, Tennessee 37830

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GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station

PROJECT TERMINATION

Date August 23, 1973

PROJECT TITLE: Magnetic Phenomena at Metal Surfaces

PROJECT NO: A-1024-004

PROJECT DIRECTOR: Dr. Stephen Spooner

SPONSOR: Atomic Energy Commission

TERMINATION EFFECTIVE: March 31, 1973

CHARGES SHOULD CLEAR ACCOUNTING BY: All charges have cleared

Final Report submitted July 2, 1973

Acceptance by AEC received August 1, 1973

Actions remaining:
Final invoice

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rm EES 402 (R10-62)

Report Number 0R0-3674-3

TECHNICAL PROGRESS REPORT

PROJECT A-1024

MAGNETIC PHENOMENA AT METAL SURFACES

By

Stephen Spooner

CONTRACT NO. AT - (40 - 1) - 3674

1 January to 31 December 1969
Issued 23 February 1970

1970

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

TECHNICAL PROGRESS REPORT

PROJECT A-1024

MAGNETIC PHENOMENA AT METAL SURFACES

By

DR. STEPHEN SPOONER

CONTRACT NO. AT-(40-1)-3674
REPORT NUMBER ORO-3674-3

1 JANUARY to 31 DECEMBER 1969

Prepared for
RESEARCH AND DEVELOPMENT DIVISION
OAK RIDGE OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISION
POST OFFICE E
OAK RIDGE, TENNESSEE 37830

TABLE OF CONTENTS

ABSTRACT

The investigation of cobalt is to continue with improved neutron mirror experiments using polarized neutrons. A new monochromatic beam facility has been designed and is nearly completed for use in this experiment. Practical problems associated with the fabrication of iron mirrors for use as neutron polarizers have been overcome. A computer control needed for the more complex experimental operations in the mirror experiment has been completed.

The same computer control, which includes a useful semiautomatic mode of operations, has been demonstrated in the measurement of copper phonons. This demonstration shows the feasibility of performing a wider range of experimentation in the study of magnetic phenomena related to cobalt.

I. INTRODUCTION

The research reported herein was carried out in the period January 1969 to December 1969. The general objective of these studies is to elucidate the relationship between magnetic properties and structure of solids with the primary undertaking directed toward magnetic surfaces. In the past year studies of cobalt films using magnetic property measurement and neutron scattering have continued. In the course of this work experimental capabilities have been improved for thin film investigations using neutron mirror techniques and new diffraction techniques for the study of related magnetic problems.

The use of neutron diffraction for the investigation of magnetism in solids is well known and because of the practical limitations of available neutron fluxes the methods of neutron scattering have been applied to bulk materials having a characteristic dimension of 1 cm. In the case of large flat surfaces it is possible to investigate the behavior of the surface region using the total external reflection of neutrons from an optically flat plane. The characteristic depth of sampling is a few hundred angstroms although the behavior is averaged over a surface of several hundred square centimeters.

The theory of the mirror experiment is discussed in detail in last year's progress report[1], but a brief review is given here. Optical principles which are largely analogous to light optics can be applied to the phenomena of total external reflection of neutrons. The index of refraction of neutrons in a ferromagnetic material is given by the equation,[2]

$$n^2 = 1 - \frac{N\lambda^2}{\pi}\left(b \pm p(o)\right) \qquad (1)$$

where N is the nuclear density, λ the wavelength, b the nuclear scattering amplitude and p(o) is the magnetic scattering amplitude in the forward direction. It is readily found that there will be total reflection of neutrons if the neutrons are incident at an angle less than a critical angle given by the equation,

$$\theta_c \pm = \left(\frac{N\lambda^2}{\pi} (b \pm p(o)\right)^{\frac{1}{2}} \tag{2}$$

It should be noticed that the nuclear and magnetic scattering amplitudes enter the expression as the sum or difference. The plus sign (+) applies to what shall arbitrarily be called the positively polarized neutrons and the negative sign (-) applies to the negatively polarized neutrons. The resulting reflectivity curve is generally the superposition of the positively and negatively polarized neutron reflectivity curves. The magnetic scattering amplitude, p, is proportional to the magnetization of the surface resolved in the surface plane. The quantity p(o) is given

$$p(o) = \frac{\gamma e^2}{mc^2} \frac{M_1}{N} \tag{3}$$

where γ is the neutron moment in nuclear Bohr magnetons, M_1 is the resolved magnetization and e, m and c have their usual meaning.

In neutron mirror studies, cobalt is of special interest since the nuclear scattering amplitude is smaller than the magnetic scattering amplitude, p(o). In this case there is only one critical angle, θ_c, so that only one polarization state is totally reflected from a cobalt surface.

Cobalt has been selected for study because (a) there have been investigations of cobalt as a polarizing mirror surface[3] and (b) magnetic

characteristics of cobalt are related to its crystalline characteristics through a strong magnetocrystalline anisotropy[4]. Neutron mirror experiments to date have indicated that evaporated cobalt films exhibit a strong anisotropy perpendicular to the film plane[5]. The magnetization is forced partially out of the plane of the mirror and thus the observed in-plane magnetization is reduced. Such an effect appears to be a function of the magnetic field strength applied parallel to the film of the mirror surface. The neutron mirror experiment can be applied to the assessment of the source and magnitude of the anisotropy and its control by metallurgical factors.

In order to achieve the requisite sensitivity in this experiment it has been necessary to enlarge on the experimental approach to the mirror experiment. Longer wavelength neutrons, use of polarized neutrons and greater mechanical stability in the arrangement of the elements of the experimental apparatus are all feasible points of improvement which have not yet been completed. In the course of developing these improvements several goals have been reached. A separate monochromated beam facility is near completion for use in the mirror experiment. The neutron polarization inverter ("flipper") has been completed and tested. Developments in the use of a computer control of experimental equipment has lead to an enhancement of our neutron diffraction capabilities which can be applied to problems related to the behavior of cobalt and strong anisotropy.

In the following report these developments are reported in more detail. A brief discussion of the computer control applied to triple-axis spectrometry is included. A paper dealing with the general aspects of computer usage given at the DECUS* meeting[6] is appended. This report represents a part of the effort by Mr. Wrege and Mr. Alderman in the development of our computer controlled experimentation.

II. EXPERIMENTAL WORK

A. Neutron Mirror Experimentation

The investigation of cobalt films is continuing with the preparations for mirror experiments with polarized neutrons. Preliminary experiments on the field dependence of the magnetization resolved in the plane of the thin film indicate a possible secondary saturation of the magnetization in the film. Low fields appear to be adequate to drive domain walls out of the film. Nevertheless a measurable fraction of the magnetization is not in the film plane. An applied field parallel to the film works in opposition to a large perpendicular anisotropy energy. A quantitative analysis of this situation will require refinements in the original experimental arrangement. Longer wavelengths will move the scattering pattern to larger angles as seen in equation (2) making geometrical collimation easier. Polarized neutrons can be used to separate the magnetic scattering from the non-magnetic scattering. Finally, mechanical stability of the apparatus particularly the electromagnet will remove an important source of experimental difficulty.

In the further investigation of the applied field effects it was found that a quantitative determination of the in-plane magnetization was not possible with the original experimental arrangement. One of the difficulties results from the use of unpolarized neutrons where there is the superposition of two reflectivity patterns. The positively polarized neutrons scatter from the cobalt film in the expected manner. The negatively polarized neutrons are transmitted through the cobalt film (since the critical angle of reflection for cobalt, θ_c, was imaginary in this case) and then scattered from the glass substrate. While the glass reflectivity pattern has served as an

non-magnetic scattering reference for comparison with the cobalt reflectivity pattern, when the resolved magnetization goes below a certain level it is not possible to observe the cobalt reflectivity curve. A further problem is that when the field strength changes there is a shift in the electromagnet pole piece due to the magnetic forces. This shift requires a tedious realignment in the experiment which make comparisons between individual reflectivity curves difficult.

As mentioned earlier, an improvement in the measurement of the reflectivity can be made through the use of a longer wavelength. In order to operate near the peak of the thermal spectrum with an acceptable wavelength resolution, we have chosen to use monochromating crystals of large lattice parameter with a monochromating angle being determined by the space limitations of adjacent experiments at the reactor. Nevertheless, wavelengths approaching 2 A can be utilized with a resultant improvement in the experiment.

The monochromated beam apparatus which is to be used in this experiment has been designed with emphasis on shielding for low neutron and gamma background[7]. Dense concrete consisting of steel punchings, iron ore (limonite) and barites sand was cast in place using wooden forms. A lead shield was placed around the monochromator. The radiation characteristics will be tested upon completion of the concrete structure of the shield. A special feature of this shield is the simplicity of construction in which blocks of concrete having characteristic dimensions of 24 inches have been cast in place. These blocks can be removed and replaced for changes in experimental and shielding requirements. In particular, the replacement of two blocks and a minor reworking of the lead shield converts the facility into a two beam unit. The blocks are easily cast with standard construction techniques.

As indicated in the last progress report[1], it was found that iron evaporated films could be used as a neutron polarizer in the mirror experiment. In the proposed experimental arrangement, the iron polarizing mirror is to be magnetized by a set of permanent magnets which generate a field of about 200 Oersteds. It is required that a very low applied field saturate the iron film. While this is not a stringent requirement, considering the magnetic softness of iron, the change in magnetic properties due to the overcoatings needed for the chemical protection of the iron were measured. In the selection of overcoating materials the neutron optical properties were taken into account. SiO, aluminum, and vanadium each have favorable neutron and chemical properties. It was found that among the three materials, vanadium coated films have the lowest planar coercive force as measured by low field torque magnetometry and also have good chemical resistance. The possible effects of anomalous diffusion[8] have not been assessed but could play an important role in the magnetic behavior of these mirrors.

In order to take full advantage of the polarized neutron method in these mirror experiments, both polarization states are used in the experiment. In this way the individual reflectivity curves for spin-up and spin-down can be compared and in a three-mirror arrangement the depolarization effects in the sample film could be assessed. A RF coil neutron-spin inverter ("flipper") which is described in the last report[1] has been completed and tested. In a triple-crystal test, using a monochromator and two iron-cobalt crystals, the flipper was placed between the neutron polarizer and analyzer crystal. The ratio between the diffracted intensity from the analyzer with the flipper off to the intensity with the flipper on was measured. After correction for

background this ratio was between 55 and 60. In the present design there is an initial relaxation in the electron current in the coil such that the averaged flipper behavior is lower than the maximum possible performance; further refinement in the apparatus may be required.

Finally, the mechanical problems related to the physical movement in the electromagnet pole pieces is to be solved by solidly embedding the lower pole piece which forms the base for the mirror mounting, rocking device and a beam limiting collimator. While the electromagnet will move as the field is changed the geometrically significant elements of the experiment with will not change relative to one another.

In summary of the optical studies of cobalt films, experimental improvements in the investigation should lead to a better determination of the field dependence of the in-plane magnetization of cobalt evaporated films. It is suspected that the magneto-crystalline anisotropy coupled with crystalline preferred orientation serve as a mechanism for perpendicular anisotropy. The secondary saturation which can be brought about through the application of the field in the plane of the film can be used as a measure of this anisotropy. The relation of these phenomena to magnetic property measurements of a conventional kind and to the metallurgical factors could be explored effectively with the anticipated experiments in which improvements are now being made. A new experiment will soon be attempted after the polarization, wavelength and mechanical improvements are complete.

B. Development and Utilization of Automatic Neutron Diffraction Apparatus

In the neutron mirror experiment several mechanical and electronic elements in the apparatus are to be automatically controlled. In order to control

the mirror rocking angle, the polarization of the neutron beam, and the position of a scanning slit (for the purpose of analyzing reflected beam shape), it is convenient to have more than a simple one-step control that is normally used in powder diffraction. A control system has been designed and completed which meets these requirements, and which extends conventional neutron diffraction capabilities. In the following, the development of hardware and software for this system is described. Neutron spectrometry techniques made possible by the control system are illustrated with results on phonon inelastic scattering measurements.

The computer hardware used in the control system includes a PDP-8/I digital computer and a general scalar-timer system, which are on intermittent loan from the Nuclear Research Center. The scalar-timer system (developed and interfaced to the processor originally for reactor related experiments), consists of four 6-decade scalars, a timer which may be set under program control, and related interfacing necessary to interrogate and communicate with the scalars and the timer. A special interface has been added to enable control of three Slo-Syn motors and a "flipper" keying signal (to invert the neutron spin polarization), and to sense limit switches to signaling dangerous equipment conditions. Details of this interface are described in the following.

The drive unit for each of the Slo-Syn motors was constructed from DEC K-series modules. The basic logic design is described in the DIGITAL Logic Handbook[9]. In this drive unit a voltage level provides the information controlling the direction of stepping and the number of motor steps upon receiving a DC level change from another input. Such an approach made the computer interface extremely simple, where a direction 'flip-flop' and a pulse

which may be sent under program control. This same drive unit is also used to run the motors from a computer independent control unit in a one-increment mode, for use when the computer is not available. This control unit will be described later.

The "flipper" keying signal is the output from a flip-flop which may be set under program control. This allows rapid switching between neutron polarization states thus compensating for time dependent drift in the quality of beam polarization. A "flipper" has been constructed which applies a radio-frequency magnetic field perpendicular to the polarization axis of the neutron beam. By adjusting the effective length of this field and the field strength, a high probability of flipping the neutron spin relative to the quantization axis is obtained.

In the computer independent mode of operation, the data recording (on a teletype) and motor moving are initiated through an intercepted stop and reset signal coming from the scalar electronics. In this mode several methods of operation may be chosen for the neutron scattering equipment. A single motor may be incremented by a preset number of pulses, thus allowing rocking curve and single crystal experiments. A two-to-one motion of two motors may be selected, thus allowing a standard theta-two-theta scan. A theta-two-theta scan with the "flipper" option allows elastic polarized beam experiments to be performed. Finally, separate control of each motor either with a hand-set increment or with continuous running can be performed for set-up operations.

The computer option is set by a switch position and connection of the communication link between the computer and the motor drive. In this mode of operation, the output of the counting equipment amplifiers is used in the computer's scalar system. All experimental control functions are then under

the control of the digital processor. At present there is 4096 12-bit words at our disposal in the computer memory.

The program control of the experiment can be handled by direct machine language programming or higher order languages depending on the specific operations of the equipment. In our case a large degree of variation is anticipated in the modes of experimental control and data handling. In order to remove the burden of machine language programming for each experimental situation a general purpose interpretive level language was used. This type of language allows rapid programming on a comprehensive, flexible level without the need for program compilation when the program is changed. The software is discussed on two levels, the machine level programming making up the interpreter itself, and the high level programming made possible by the interpreter.

The interpreter was assembled by adding special functions to the FOCAL language (described in a rather sophisticated level in the appended paper by Wrege[6]) for running the motor stepping operations and using the scalers. The interpreter is made up of many subroutines and text handlers which are designed to handle every conceivable operation the user may wish to perform. The user may put these functions together in the order and manner he wishes to run a given experiment. Only the symbols for the program are stored, each statement in the program is then interpreted at execution time and the appropriate subroutine is called without translation into machine language instructions. In this way a short simple statement is sufficient to control a complex experimental operation.

FOCAL programming is set up with numbered statements which can be grouped together for access as a separate function. For example, one group of statements translates angular settings of the diffractometer to motor steps and calls the subroutine to step the motors. Another group runs the monitor and detector scalars to a preset monitor count. Still another group calculates the angles necessary to reach a particular point in reciprocal space. These three groups of statements may be used in a large class of experiments, requiring only a small amount of programming for each particular experiment. For example, one may change from a "constant-Q" to a "constant E" to an elastic scan in reciprocal space by changing a single line of coding. In fact, to sample along an arbitrary directed line in reciprocal space takes only modification of two or three lines of the indirect program.

C. Application of Computer Controlled Experimentation to Neutron Spectroscopy

The study of magnetic phenomena with neutron scattering can be carried out with (1) two-axis diffraction analysis of structure using polarized neutrons and (2) triple-axis scattering analysis of dynamics in the magnetic system which reveal the magnetic interactions in a direct way. From a practical viewpoint the single most important phenomena in cobalt is the magnetocrystalline anisotropy which is thought to depend on crystal field, spin-orbit coupling and dipolar interactions[10]. Experiments related to the problem of anisotropic magnetic behavior shed light on this important aspect of the cobalt behavior. For this reason the possibility of performing spectroscopy with triple-axis techniques has been explored using the measurement of phonon scattering from copper as a test of the computer controlled experimentation. Below we show the feasibility of performing such experiments, and

arrangements for the joint exploration of the dynamics of magnetic systems using the facilities of Georgia Tech and the Oak Ridge National Laboratory[11] are being made.

The coherent scattering from a solid is governed by a momentum and energy conservation so that the momentum change and the energy change in scattering of neutrons is related to interactions of excitations such as phonons and magnons[12]. The relations are written,

$$\frac{\hbar^2 k^2}{2m} - \frac{\hbar^2 k'^2}{2m} = \pm h\nu \tag{4a}$$

$$k - k' = \tau + q \tag{4b}$$

where k and k' are the incident and scattered wave vectors of the neutrons, τ is the reciprocal lattice vector, q is the excitation wave vector, and $h\nu$ is the energy of the excitation which may be created or destroyed in the process of scattering. In order to measure the energy and momentum of a given excitation it is convenient to control the diffraction apparatus so that the wave vector of the excitation is fixed while the energy of the scattering is scanned. The peak intensity of such a curve gives the value of the energy of the excitation and the momentum is the constant value maintained by the control of the diffraction geometry. This method, called the constant-Q method, is described by Brockhouse[13] and has been used by many experimentalists. In general the incident neutron energy is controlled by adjustment of the monochromator while the scattered energy is selected by control of an energy analyzing crystal set in the path of the neutrons scattered from the sample. The control of crystal orientation and scattering angles serves to determine the remaining conditions implied in the above equations.

In our apparatus the incident energy was fixed by the wavelength (1.098 A) of the neutrons scattered from the (200) planes of a deformed copper crystal. The specimen was a copper crystal 1 cm thick with a flat face 4 cm on a side. The energy analyzer crystal was a hot-deformed germanium crystal[14] in which the (400) planes were used in a transmission geometry. The mosaic spread of the copper crystal was approximately 20' and collimators having a nominal cross fire angle of 40' were used between the monochromating crystal and the specimen and between the specimen and the analyzer crystal. The neutron flux at one megawatt at the sample position was 0.8×10^6 neutrons/cm^2 sec.

A reasonable peak-to-background ratio was obtained only after improvements in the shielding were made. The neutrons emanating from the monochromator shield were brought under control with a shielding wall made of boron oxide/paraffin bricks. Other experiments using the horozontal beam ports contributed an important fraction of the background counts so that the counter shield had to be improved. A boron carbide shell of 12 inch diameter bonded with epoxy resin formed a shield around the detector. With the addition of paraffin around the boron carbide, the background rate was brought down to approximately 1.5 counts per minute. Background with the reactor-down was less than 0.2 counts per minute.

Our phonon experiments were designed to provide a comparison with the work of Nicklow, et al. at Oak Ridge[15]. Transverse phonons along the [100] direction and longitudinal phonons along the [111] direction have been measured with sufficient resolution for comparison with the energies given by the Oak Ridge workers. The transverse phonons along the [100] branch emanating from the 331 reciprocal lattice point gave the most intense phonons

intensities. This is due in part to the focusing conditions of the particular experiment which we have begun to explore using the theory developed by Cooper and Nathans[16] and by Neilson and Moller[17]. For the $\xi 00$ phonon with $\xi = 0.4$, the peak intensity was 190 counts in 15 minutes with a background of 30 counts in 15 minutes. The energy width of this peak was 0.5×10^{12}cps compared with 0.16×10^{12}cps for the same phonon measured by the Oak Ridge workers. The higher degree of crystalline perfection of the Oak Ridge crystal accounts for part of this difference.

These experiments were done in the constant-Q mode under the control of the digital computer. With the feasibility of neutron spectroscopy demonstrated at a one megawatt power level the prospects for further experimentation in this area at five megawatts look very good. The exploration of magnetic excitations in solids are much more difficult to perform than the lattice dynamics experiments, however. An arrangement with Oak Ridge can be made in which short term use of the higher flux facilities can be made with Georgia Tech personnel who have been trained in neutron spectroscopy at the Georgia Tech reactor. Furthermore, there are useful aspects of many such experiments which can be explored usefully at a lower flux facility.

III. SUMMARY

The investigation of cobalt has continued with emphasis on improvement of neutron mirror experiments using polarized neutrons. A new monochromatic beam facility has been designed and is nearly completed for use in this experiment. Practical problems associated with the fabrication of iron mirrors for use as neutron polarizers have been overcome. A computer control needed for the more complex experimental operations in the mirror experiment has been completed.

The same computer control, which includes a useful semiautomatic mode of operations, has been demonstrated effective in the measurement of copper phonons. This demonstration shows the feasibility of performing a wider range of experimentation in the study of magnetic phenomena related to cobalt.

In the mirror experiments it is anticipated that the study of the in-plane magnetization as a function of field can be related to the strength of anisotropy. Studies of depolarization effects which are now possible using polarized neutrons can be related to defect structures and other metallurgical factors. The use of neutron spectroscopy in order to measure magnetic dynamics approaches the fundamental problems most directly and a cooperative undertaking with Oak Ridge makes this possible.

IV. IDENTIFICATION OF PERSONNEL

The following have participated in the project during the period covered by this progress report.

Dr. Stephen Spooner, Assistant Professor of Chemical Engineering (Metallurgy Program) is Senior Investigator.

Mr. B. R. Livesay, Research Physicist, is engaged in the magnetic studies with the torque magnetometer. He is currently pursuing doctoral studies in the Metallurgy Program.

Mr. D. E. Wrege, Graduate Student in Physics, is the principle graduate student engaged in neutron scattering studies and has been responsible for computer programming.

Mr. J. C. Alderman, Research Engineer, is supplying part-time help towards automatic control of neutron facilities and computer data handling techniques.

Mr. J. C. Meaders, Assistant Research Engineer, is responsible for thin film preparations.

Mr. A. J. Foltman, Graduate Student in Nuclear Engineering has given assistance in the construction of neutron shielding.

Mr. R. Elliott, Graduate Student in Physics, is assisting in torque measurements and magnetic force probe measurements.

Mr. R. Patchin, Graduate Student in Textiles. He supplied part-time laboratory assistance. Resigned at end of summer.

Mr. J. W. Lynn, Graduate Student in Physics, is assisting in shielding work.

Mr. T. H. B. Sanders, Graduate Student in Metallurgy, is assisting in structural aspects of magnetic problems.

Mr. R. Altman, Graduate Student in Physics, is on a U. S. Steel fellowship and is assisting in neutron spectroscopy measurements.

V. TRIPS AND VISITS

1. Dr. Spooner traveled to Oak Ridge, Tennessee, to attend the Oak Ridge National Laboratory Solid State Division information meeting on 15 April.

2. Dr. Spooner and Mr. D. E. Wrege traveled to Oak Ridge, Tennessee, to prepare some hot pressed germanium crystals in collaboration with R. M. Nicklow of the Solid State Division of ORNL on 20 June.

3. Dr. Spooner traveled to Stony Brook, Long Island, on 29 and 30 August, for the Topical Meeting on Neutron Scattering of the International Crystallographic Union Meeting.

4. Dr. Spooner and Mr. B. R. Livesay attended the Fifteenth Annual Conference on Magnetism and Magnetic Materials held in Philadelphia, Pennsylvania, on 18 November through 21 November.

VI. INCIDENT REPORT

There were no unusual incidents during the period covered by this report.

Respectfully submitted,

S. Spooner
Senior Investigator

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APPENDIX I

Report Number ORO-3674-5

FINAL REPORT

PROJECT A-1024

MAGNETIC PHENOMENA AT METAL SURFACES

By

Stephen Spooner

CONTRACT NO. AT-(40-1)-3674

1 January 1971 to
31 March 1973

1973

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

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FINAL REPORT

PROJECT A-1024

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1 January 1971 to 31 March 1973

Prepared for
RESEARCH AND DEVELOPMENT DIVISION
OAK RIDGE OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISSION
POST OFFICE E
OAK RIDGE, TENNESSEE 37830

TABLE OF CONTENTS

I. ABSTRACT

Cobalt and cobalt alloy thin film property studies have continued on the basis of planar torque magnetometer measurements. Epitaxial effects have been clearly shown in the 6-fold planar torque curves in instances of demonstrated epitaxial relation between evaporated films and copper single crystal substrates.

The principal use of neutron scattering has been in the study of the highly anisotropic $FeCO_3$ with elastic and inelastic neutron scattering experiments. In addition to finding of a magnetic excitation reported in the last progress report, we have found magnon-phonon interactions having a symmetry dependence indicating a crystal field modulation effect. Elastic scattering measurements of magnetic long-range order have been compared with Monte Carlo calculations and in this instance an Ising model Hamiltonian proved to produce a good correspondence. The current problems in the understanding of $FeCO_3$ are summarized in this report.

II. INTRODUCTION

The initial experimental investigations of this program were based on the study of cobalt films by neutron scattering and torque magnetometer measurements.[1 2 3 4] These studies showed that the magneto crystalline anisotropy acting in conjunction with polycrystalline texture was responsible for forcing the magnetic moment out of the film plane. The phenomena of anisotropy became a primary and common factor in the subsequent research. Thin film work continued with studies of expitaxial effects of cobalt and cobalt alloy films deposited on copper single crystal substrates.[5] Neutron mirror experiments were extended but technical difficulties forced us to abandon that use of neutron scattering. Instead, the major use of neutron scattering was in conventional elastic scattering studies at GTRR[6 7 8 9 10] and inelastic scattering at the reactor of Oak Ridge National Laboratory.[10 11] Since the last reporting period neutron scattering studies have focussed on $FeCO_3$. In this material, single ion anisotropy due to crystal field and spin-orbit effect clamps the magnetic moment along the trigonal axis. More significantly, the magnetic Hamiltonian describing this system appears to be equivalent to the Ising model.[11 12 13] Our work on this system has led to fruitful cooperation with our faculty in the School of Physics, members of the physics faculty in the Physics Department at the University of Georgia and the Solid State Division at Oak Ridge National Laboratory. While the major effort has moved away from an interest in metal surfaces, a sustained interest in magnetic anisotropy has remained a motivating theme in this work.

The following progress report discusses our work in two parts. The first part summarizes the work on the magnetic mirror and on cobalt and cobalt alloy films. Our most recent results on iron-cobalt alloy films are tabulated.

In the second part the work on $FeCO_3$ is discussed extensively. Progress on the inelastic scattering work at ORNL is reviewed and study of the magnetic transition at GTRR is discussed in greater detail. Many problems remain for the analysis of $FeCO_3$ and the present state of understanding is reviewed.

III. EXPERIMENTAL WORK

A. Thin Film Studies

1. Magnetic Properties

Magnetic properties of thin films have continued to be studied with torque-magnetometer measurements. The six-fold planar anisotropy of cobalt films deposited on (111) copper substrates was studied in relation to epitaxial effects. The results of studies of cobalt and cobalt-6% iron films were reported at the Denver magnetism conference.[5] Six-fold planar anisotropy was observed only in epitaxially deposited films. Neither six-fold symmetry nor evidence for epitaxy were found in the 6% iron alloy films.

The conditions for epitaxial deposition of cobalt are controlled by the stability of the HCP and FCC structures and substrate-film lattice misfit. Small volumes of FCC cobalt are known to be stable at room temperature such as cobalt precipitates in copper and films evaporated onto a variety of substrates.[14] [15] [16] [17] Our explorations of the effect of substrate temperature show that epitaxial films can be produced on copper single crystals held at 300°-400°C during slow evaporation. The lattice misfit is generally thought to be accommodated by interfacial dislocation arrays,[15] [16] especially in the case of thin films. As film thickness increases loss of lattice coherency is expected. The tendency for little or no epitaxy in thick films is consistent with dislocation processes assisting the conversion of FCC cobalt to the more stable HCP structure. It is not clear why 6% iron alloy films are not formed epitaxially even though the alloy should be stable down to room temperature.

Low concentration iron alloys of cobalt have become increasingly interesting with the discovery of a previously unrecognized phase in the range of 1% to 4% iron in cobalt.[18] [19] From 0 to 1% Fe there exists the HCP (ABAB...)

structure, from 1% to 4% FE a double-hexagonal structure (ABAC...) exists and the FCC structure exists from about 4% up to 10% iron. Our most recent efforts on thin film study have concentrated on the study of these alloy materials evaporated on copper substrates. Both (111) copper single crystal surfaces and (100) NaCl surfaces with evaporated copper have been used as substrates. These substrates were heated to 300-400°C for 6-24 hours prior to and during evaporation.

The copper crystal substrates were wafers of about 2.5 cm diameter having thicknesses 0.5 - 1.0mm. The steps used to prepare the copper single wafers are listed below:

a) One inch diameter bulk copper crystal rods (99.999%) were sectioned parallel to a (111) plane by spark slicing.

b) Oriented bulk crystal sections were radiation hardened in the Georgia Tech reactor using 10^{17} - 10^{18} neutrons/cm^2 in order to minimize damage to the crystal during subsequent preparation steps.

c) Uniform thin wafers were spark sliced from the bulk sections using specially developed mounting and alignment procedures to provide uniformity and minimum damage to the wafer.

d) The wafers were mechanically polished to remove irregularities introduced during spark slicing. Specially designed polishing blocks supported the wafers during this step and permitted the thickness to be selected to 0.001 inch with a comparable uniformity.

e) The wafers were electropolished in orthophosphoric acid using a cell geometry which maintained the flatness of the large surface.

f) The wafers were vacuum annealed at above 1000°C for more than 6 hours to remove the radiation hardening and possible damage to the crystal.

Films were deposited in vacuum at pressures of about 1×10^{-6} torr. Film thicknesses and deposition rates were determined using a quartz crystal thickness monitor which had previously been calibrated for the specific geometry employed for these depositions. The distance of the source from the substrate was about 15 cm so that films were uniform over the 2 cm diameter mask employed here.

Magnetic property measurements were carried out using a sensitive automatic torque magnetometer described earlier.[20] During the past year a digital rotational drive was added to one of the Varian electromagnets so that the rotation of the field about the specimen could be programmed. This proved necessary since slow and uniform rotation of the field is required to eliminate the introduction of background torques due to induced currents in the copper substrates.

Anisotropy constants of the film materials were obtained by Fourier analysis of high field torque curves measured by rotation of the field vector in the plane of circular films. The torque vector was measured normal to the surface of the film. The analysis was carried out for the magnetocrystalline anisotropy energy expanded in terms of the direction cosines[(a)] for a cubic lattice structure. The crystallographic orientation of the film planes employed in these investigations were (111) and (100). Therefore for a (100) plane with θ measured in the plane relative to the $[00\bar{1}]$ direction

$$\frac{dE}{d\theta} = \frac{K_1}{2} \sin 4\theta.$$

For a (111) plane with Θ measured relative to $[1\bar{1}0]$

$$\frac{dE}{d\theta} = \frac{K_2}{18} \sin 6\theta.$$

The measured torque per unit volume, L, is defined by $L = -dE/d\theta$.

In addition to the above magnetocrystalline anisotropy terms,

uniaxial anisotropy of a different origin was always found and is represented analytically as

$$L_u = K_u \sin 2\theta.$$

A summary of the anisotropy constants measured for cobalt and Co-Fe alloy films is provided in Table 1. The pure cobalt films are saturated at fields between 3000-4000 oersted. However, Co-3.5%Fe films required greater than 8000 oersted for saturation. The rotational hysteresis of the pure cobalt films at 500-1500 oersted fields was consistent with that resulting from stripe domain models. At very low fields the phase of the $\sin\theta$ behavior was completely determined by the direction of the last applied high field.

Electron diffraction investigations were carried out in the back reflection mode for the films grown on copper crystal wafers. Films deposited on the copper coated NaCl crystals were floated off the salt crystals and examined by transmission electron microscopy. Examinations of the lattice misfit accommodating dislocation network at the Cu-CoFe interface were also carried out on these films. The film deposition parameters were satisfactory for the growth of FCC single crystal films of pure cobalt on the (111) copper crystal wafers. However, a number of attempts to grow single crystal Co-6%Fe films did not produce films having electron diffraction patterns corresponding to a single crystal material. The Co-4.5%Fe and Co-3.5%Fe alloy films on copper coated NaCl crystals resulted in uniformly good single crystal electron diffraction patterns.

TABLE 1

Summary of Torque Magnetometer Results

Film Thickness (Å)	$K_2(10^4$ erg/cc)	$K_u(10^4$ erg/cc)	Comment
2750	-7.3	4.1	cobalt on $C_u(111)$
2100	-0.71	0.52	"
1200	No	5.1	"
820	-1.6	0.62	"
350	No	25.	"
1430	No	1.1	6%Fe alloy on $C_u(111)$
1250	No	4.8	"
350	No	10.0	"
2000	Small	2.2	4.5%Fe alloy on Cu(111)
150	-5.3	0.7	"
1500	No	1.2	3.5%Fe alloy on Cu(111)
800	Small	5.0	"
	$K_1(10^4$erg/cc)	$K_u(10^4$erg/cc)	
150	2.4	3.2	4.5%Fe alloy on Cu on NaCl(100)
800	0.44	0.39	3.5%Fe alloy on Cu on NaCl(100)

2. Neutron Mirror

Work on the neutron mirror experiments was discontinued as of May 1972 for reasons of available manpower and a decision to concentrate on conventional neutron diffraction work described in part B in the section on experimental work. Since the last reporting period, refinements in the experimental set up were made in monochromating technique, beam filtering and in the design of the two mirror apparatus. A small graphite crystal replaced the germanium crystal as a monochromator thus producing a somewhat longer wavelength and a 50% increase in intensity. Nevertheless, the experiment has been plagued with the problem of a fast neutron background. A synthetic quartz crystal was used as a beam filter but with a significant loss in thermal neutron intensity. The greatest difficulty encountered in the experiment was in the use of the electromagnet for studies of field dependence of film saturation. Strong fields gave rise to small but readily detectable mechanical motion in various parts of the mirror apparatus. Such mechanical problems caused us to redesign the magnetic mirror mounting with a tortional mount and we removed all ferromagnetic materials in the construction. Within the time allotted and particularly with the departure of the student worker who was familiar with the experiment we could not test the improved two mirror experiment.

B. Magnetic Anisotropy in Iron Carbonate

1. Introduction

Magnetocrystalline anisotropy arises from coupling between the magnetic moment and the crystalline lattice and such anisotropy is generally mediated by spin-orbit interaction. The spin-orbit interaction energy in metals is small relative to the d-electron band width and therefore quantitative treatment of magnetic anisotropy in metals is difficult to study. In non-metallic salts, however, it is possible to work with discrete energy levels which are subject to calculable crystal field, spin-orbit and exchange effects. In the case of $FeCO_3$ crystal field interactions dominate the Fe^{+2} energy level splittings in such a way that a low lying (magnetic) doublet is split into a 5-fold manifold by spin-orbit interaction. In such a scheme Kanamori[11] showed that x and y components of the moment are quenched and that the moment is effectively clamped along the trigonal axis of the crystal. Under these circumstances it was shown that the magnetic Hamiltonian could be replaced by the Ising model. Thus considerable simplification results in the analysis of magnetic behavior.

The research we have undertaken on $FeCO_3$ focussed on the Ising behavior of the magnetic system. An important prediction emerging from the theory of the Ising model is that magnetic excitation (magnons) are strictly localized, i.e., they do not propagate because there can be no coupling between adjacent moments through x and y moment components. This is manifested through inelastic neutron scattering as an excitation with no momentum transfer dependence --- in other words the excitation exhibits no dispersion. Predictions of the behavior of sublattice magnetization and spin correlations can not be calculated by rigorous analytic methods although computer

calculations based on the Monte Carlo technique[21] provide good approximations to expected behavior. The theoretical problems associated with the 3-dimensional Ising model are made more difficult by the inclusion of second and higher neighbor interactions. Fortunately the Monte Carlo technique readily incorporates such interactions into its calculations. We have used those Monte Carlo calculations for the analysis of the temperature dependence of sublattice magnetization. Throughout our research we have been concerned with the validity of the electronic energy level scheme on which the Ising model assumption is built. Evidence from several sources suggests that Kanamori's model for Fe^{+2} is correct for $FeCO_3$. Further work on this last question is needed.

2. Inelastic Scattering Experiments

Since the last report, two important observations of inelastic scattering effects have been made. First, the unusual dependence on phonon symmetry in the magnon-phonon mode crossing has been confirmed for two symmetry directions of phonon propagation. Second, a low lying magnetic excitation, first observed in infrared spectroscopy[22], have been observed in separate inelastic scattering experiments on our specimen of $FeCO_3$[30]. The latter observation has been confirmed as a manganese impurity mode that does not appear in the neutron spectra of a pure synthetic $FeCO_3$ powder. The identification of this low lying mode as an impurity effect removes a degree of uncertainty in the interpretation of the energy level structure of Fe^{+2} in $FeCO_3$.

The phonon-magnon interaction giving rise to the observed mode crossing effects was analyzed phenomenologically in terms of interaction linear in magnon and phonon operators and appears to be explained by recently proposed crystal field perturbation effects[23,24]. The low lying magnetic mode initially gave reason to doubt the Kanamori theory for Fe^{+2} on which the Ising model approach was based. Fortunately, analysis of this mode in pure synthetic

powders shows that this excitation is associated with an impurity mode on manganese. These effects are fairly well understood but further work on both the phonon-magnon interaction and the manganese impurity mode would be profitable.

The magnon-phonon interaction is responsible for the removal of degeneracy at the point of crossing of the magnon and phonon modes. The modes are modified at the region of crossing into modes of mixed phonon and magnon character. The observation that only certain phonon modes exhibited such an interaction at the point of crossing was striking. One would normally expect that modulation of the distance between interacting moments by a phonon would change in the exchange coupling interaction. Therefore, all phonons would have a magnon-phonon interaction that would remove the degeneracy at points of magnon and phonon crossing. The recent crystal field perturbation theory explains the observed phonon interaction symmetry qualitatively on the basis that only certain disturbances to the environment of Fe^{+2} will affect the crystal field in a way that changes electron energy levels. Thus only one of the two tranverse modes propagating along the $\{1\bar{1}0\}$ direction is non-degenerate with the magnetic excitation.

A quantitative prediction of the crystal field perturbation is that the magnon-phonon interaction is linear in the phonon and magnon operators. This prediction was tested in a heuristic treatment of the excitation energy variation and intensity variation in the vicinity of the mode crossing. The details of theoretical development are given in Wrege's thesis. The results are shown in Figure 1 where the variation of excitation energies is well fit by the curves calculated with a single parameter for the magnon-phonon coupling for each direction for phonon propagation. An illustration

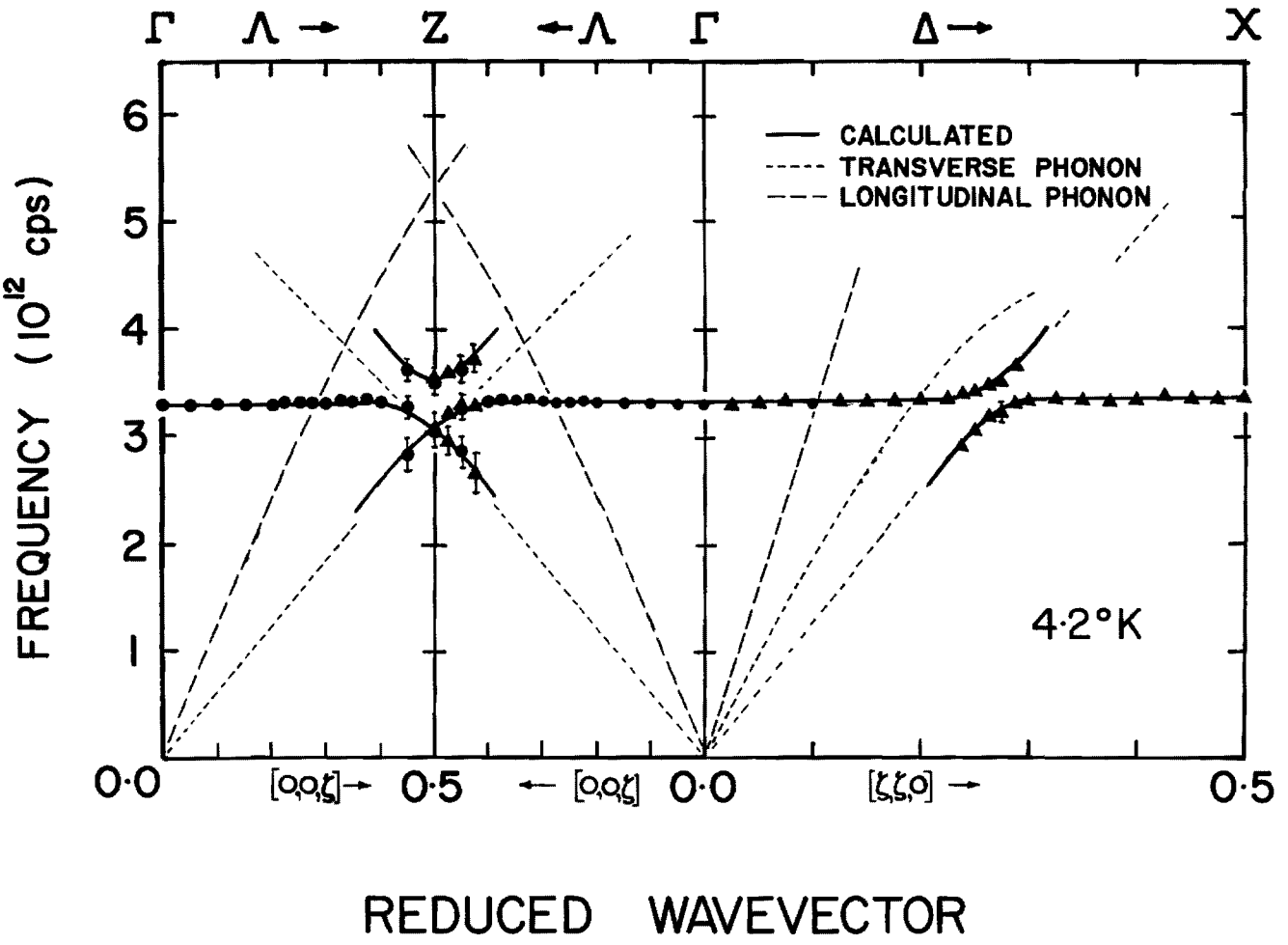

Figure 1. Magnetic and Lattice Excitations in $FeCO_3$.

of the fit achieved for the excitation intensities is given in Figure 2 of the paper presented at the Chicago Magnetism Conference.[8]

In principle it is possible to calculate the phonon-magnon coupling parameters from the theory described by Lovesay.[23] However, accurate wave functions describing the Fe^{+2} ion are needed. Unfortunately, there is not enough information on the energy level scheme for Fe^{+2} in $FeCO_3$ to check the assumptions used by Kanamori in his discussion of the single ion state of Fe^{+2}. There is currently underway a calculation of wave functions and energy levels which should verify from first principles where Kanamori's assumed energy level scheme is correct. Experimentally, there is no evidence to contradict the assumed scheme. Thus, it is hoped that the new calculations will not only substantiate the Kanamori model but will provide the needed wave functions to calculate the magnon-phonon coupling parameters.

Another application of the wave-functions is in the calculation of the magnetization form factor for Fe^{+2} in $FeCO_3$. We have collected a limited set of magnetic Bragg diffraction intensities from our crystal and we understand that a more comprehensive effort is underway at Cambridge[25] to analyze the magnetic form factor of a pure synthetic crystal.

A brief comment on the interpretation of the magnetic excitation observed in $FeCO_3$ is appropriate before leaving the subject of inelastic scattering. To our knowledge our inelastic neutron scattering results on the magnetic excitation in specifically $FeCO_3$ are unique, the observed lack of q-dependence in the excitation has not been seen in any other Fe^{+2} system. In $FeCl_2$[26] the magnetic excitation for q along the trigonal axis has no dispersion but in the plane perpendicular to the trigonal axis there is an appreciable variation with q. In FeF_2[27] the dispersion is over a small fraction of the average magnetic excitation energy but is readily observed.

However, in $FeCO_3$ the estimate of the lower limit for dispersion (or q-dependence) in the $FeCO_3$ excitation depends on the assumed of the spin-orbit interaction energy. The observed excitation in $FeCO_3$ can be crudely understood as an exciton in which a transition is made between electronic states in the low lying manifold where both spin-orbit splitting and exchange effects define the excitation energy. The transition observed with neutron scattering is selected as the lowest allowed transition involving an angular momentum change of one rather than a simple spin flip (which involves a nominal angular momentum change of 6). If a dispersion relation common to antiferromagnetics is included, the excitation energy is written,

$$E^2 = (\{E_{ex} + E_{s-o}\}^2 - C\, E_{ex}^2\, \{1/z \sum_{\delta}^{z} e^{i\vec{k}.\delta}\}^2)^{1/2}$$

where E_{ex} is the exchange coupling energy, E_{s-o} is the spin-orbit energy, the summation is made over z first neighbors and c is a multiplicative parameter scaling the relative contribution due to dispersion. When this form is used in a least-squares fit to the neutron inelastic scattering data on the excitation, the parameter c is less than 0.10. This limit appears to be largely that established by statistics and depends on the value assumed for E_{s-o}. The value for E_{s-o} was taken to be the nominal value of 2.7 Thz. We have subsequently found that E_{s-o} may be less (approximately 2.6 Thz) thereby rendering the above limit of observed dispersion conservatively high.

In summary, experiments on inelastic neutron scattering from $FeCO_3$ have proven to be unexpectedly rich in solid state phenomena that could usefully be pursued further. The observation of a dispersionless magnetic excitation to this system corroborates the assumption of Ising model behavior. By the same token the no information on the exchange coupling can be obtained

directly from the excitation energy. Thus, elastic scattering investigations of the sublattice magnetization and possibly the short-range correlation coefficients above T_n are essential to the study of the magnetic interactions in $FeCO_3$. These elastic scattering investigations are discussed in the following sections on sublattice magnetization and paramagnetic scattering.

3. Sublattice Magnetization

Calculations of the sublattice magnetization of 3-dimensional Ising antiferromagnet as a function of temperature have been carried out with a Monte Carlo method implemented by Dr. D. P. Landau at the University of Georgia.[21] A report of the work comparing measured sublattice magnetization with the Monte Carlo calculations was given at the Denver magnetism conference.[10] The two neighbor Hamiltonian employed in the calculation is written,

$$H = K_{nn} \sum_{i\ j} \sigma_i^2\ \sigma_j^2 \ + K_{nnn} \sum_{i\ k} \sigma_i^z\ \sigma_k^z$$

where K_{nn} is the nearest neighbor exchange coupling interaction, K_{nnn} is the next nearest neighbor exchange coupling interaction and σ_j^z is the z-component of the moment at the ith site. The operator σ^z assumes values of ± 1 as required by the Ising model. The calculations were carried out for a range of interaction ratio values from -0.4 to 0.2. For each such interaction ratio it was necessary to extrapolate the resulting sublattice magnetization as a function of the size of the spin lattice size to infinite lattice size.[6]

The experimental measurements of sublattice magnetization were based on integrated intensities corrected for extinction and background. When the experimental intensity data were compared with the Monte Carlo results, the best agreement resulted when the interaction ratio, K_{nn}/K_{nnn}, was -0.4. The smoothed Monte Carlo results for this interaction ratio and the normalized integrated intensity data are shown in Figure 2.

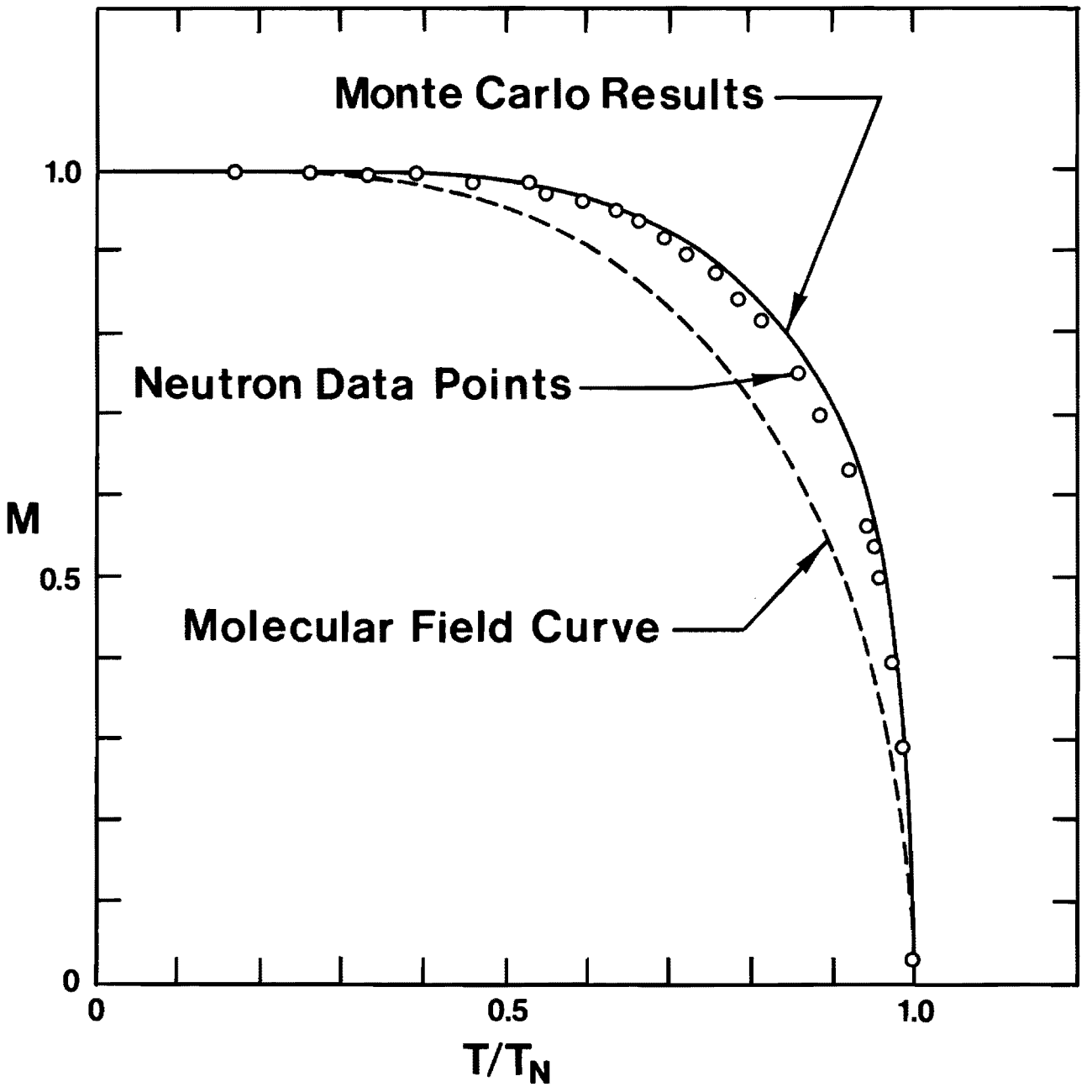

Figure 2. Sublattice Magnetization in $FeCO_3$.

The agreement between experimental data and Monte Carlo calculations is dependent on the interaction ratio alone. The two interaction energy values can be obtained by interpretation of the Neel temperature and critical field value. Such an interpretation yields an adequate agreement with our calculations.[6]

Study of critical phenomena is rendered nearly impossible in the sample of poor crystalline perfection and impurity content at our disposal. Nevertheless, magnetic properties can be calculated fairly well at temperatures away from the critical region as a function of impurities. A manganese content corresponding to 6% cation substitution exists in our sample. The Monte Carlo calculation was modified so that 6% of the moments were replaced by manganese (Ising) moments. The parameters associated with Mn-Fe and Mn-Mn were estimated from magnon measurements in $MnCO_3$[28] and the observed impurity mode energy.[22,29] Preliminary results of the Monte Carlo calculations show that introduction of these impurities can account for a lowering of the Neel temperature and an improved fit to our sublattice magnetization data.

4. Paramagnetic Scattering

A further check on the exchange coupling values can be made through a comparison between diffuse scattering cross sections and calculated cross sections evaluated from spin correlations calculated from Monte Carlo calculations. This method of analysis is by far more feasible than the evaluation of spin correlations through Fourier inversion of diffuse scattering. We have been able to do preliminary diffuse scattering measurements only although a number of interesting features can be reported.

The single ion anisotropy which clamps the spin along the trigonal axis is applicable to the iron moment as long as it occupies the low lying

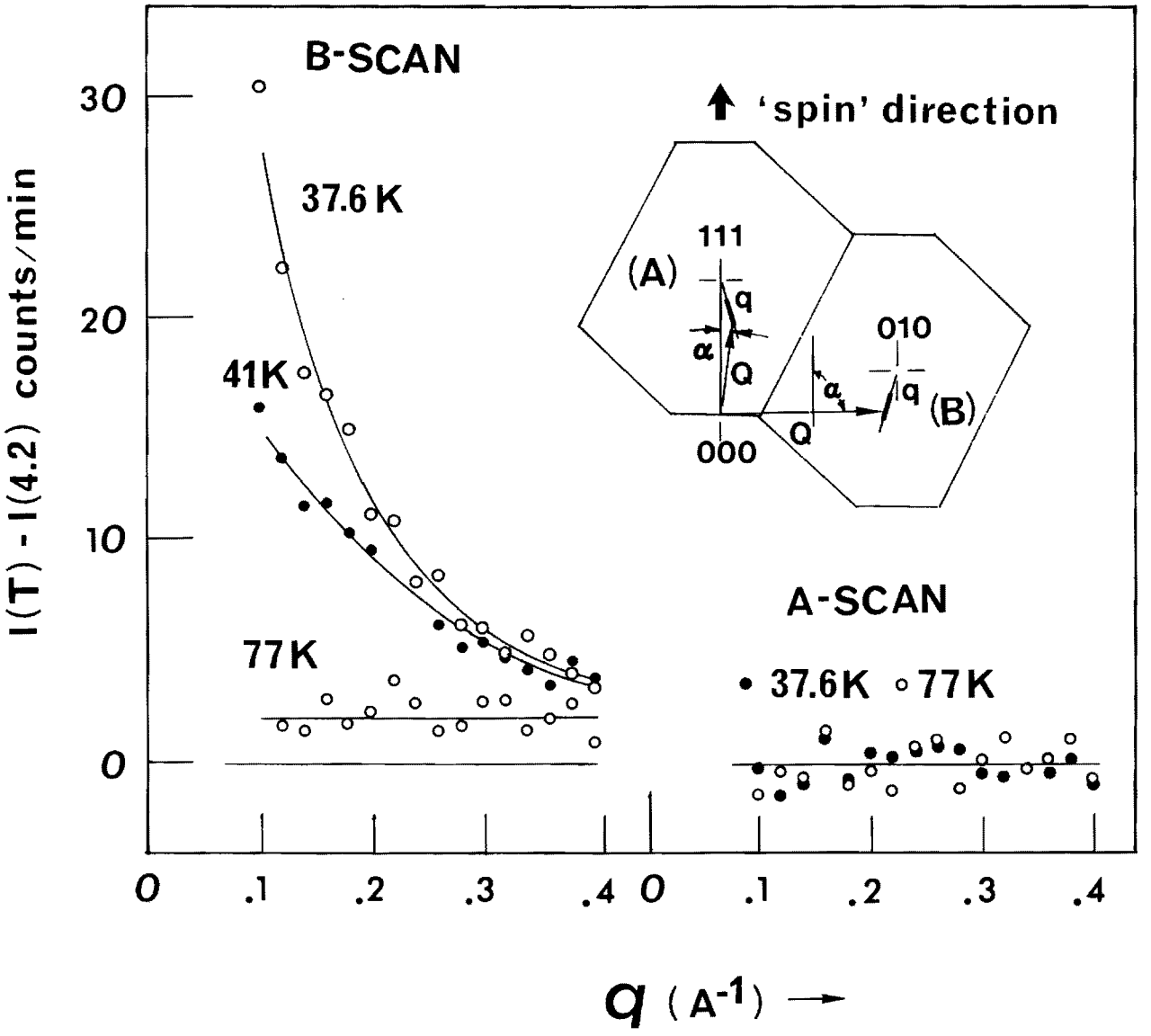

Figure 3. Paramagnetic Scattering in $FeCO_3$.

manifold of electronic states. As temperature rises, states above the ground state are thermally populated with a decrease in the z-component moment. Within the manifold the moments of each state are clamped along the trigonal axis and the moment will have a different magnitude in each level in the manifold. The persistence of single ion anisotropy above the ordering temperature is readily verified by the examination paramagnetic scattering intensity. If the moment is clamped along the trigonal axis even though it is disordered with respect to its neighbor, the paramagnetic cross section will be proportional to $\sin^2\alpha$, where α is the angle between the diffraction vector and the trigonal axis. Such an effect is shown in Figure 3. Short range magnetic order scattering along the (111) direction in Brillouin zone (about the 100 Bragg position) is shown in contrast to the same run taken in another Brillouin zone (about the 111 Bragg position). The difference between the two curves is explained by the fact that the angle α is approximately 90° in the first case and zero in the other case. This same paramagnetic scattering anisotropy is found at liquid nitrogen temperatures as well.

In consideration of the special nature of Ising system scattering it was decided to measure the strictly elastic scattering from $FeCO_3$. This procedure is additionally justified on the basis that impurity mode scattering and phonon scattering can be eliminated. The z-z spin correlations give rise to strictly elastic scattering which contrasts to the behavior in the Heisenberg systems in which paramagnetic scattering (in the vicinity of the critical temperature) can have a finite distribution of energy. A triple-axis configuration was used in which the analyser was set for elastic scattering. Tests were made with available collimators and monochromator crystals. An arrangement which used a germanium monochromator and a copper was selected.

The resolution ellipsoid was satisfactory for the measurement of scattering in terms of reciprocal space resolution and energy discrimination against the low lying manganese impurity mode.

The preliminary data demonstrate anisotropy of paramagnetic scattering and the diffuse scattering distribution may be used for initial tests of Monte Carlo spin correlation calculations. It is clear that more diffuse scattering data in the paramagnetic region ought to be obtained. Experimental improvements based on the use of graphite monochromating and analysing crystals with a graphite filter and higher flux would make such an experiment more feasible.

IV. IDENTIFICATION OF PERSONNEL

The following have participated in the project during the period covered in this report:

Dr. Stephen Spooner, Associate Professor of Chemical Engineering, (Metallurgy Program) is Senior Investigator.

Dr. B. R. Livesay, Research Scientist, is engaged in the magnetic property studies of thin films.

Dr. D. E. Wrege, Research Scientist, was engaged in neutron scattering studies in pursuit of doctoral studies and since 1971 has been engaged as advisor on data analysis and computer control of neutron scattering equipment used at Georgia Tech.

Mr. R. F. Altman, Graduate Student in Physics, is engaged in neutron scattering studies and Monte Carlo investigations of iron carbonate.

Mr. J. C. Alderman, Research Engineer, supplied assistance in developing automatic control and computer facilities for data handling up to June, 1971. His functions were assumed by Dr. Wrege at that time.

Mr. George Rothe, Physics Undergraduate, worked on the neutron mirror equipment and assisted in neutron diffraction studies until 1972.

Mr. Lamar Brown, Physics Undergraduate, assisted in the performance of torque magnetometer studies of cobalt until 1972.

Mr. Larry Phillips, Research Technician, assisted in work on specimen preparation and torque magnetometer studies from November 1972 to March 1973.

Dr. Remy Lemaire, Consulting Scientist, came to Georgia Tech in connection with a combined visit to Georgia Tech and the University of Georgia. During his stay in November 1971 he conferred with Dr. Spooner and Dr. Livesay on rare earth cobalt compounds.

Dr. Olaf Steinsvol, Consulting Scientist, physicist at the nuclear research center at Kjeller, Norway and then currently visiting scientist at ORNL, visited in July 1972 for the purpose of advising us on the design of the resolution and monochromator system for our work on quais-elastic scattering measurements on iron carbonate.

Dr. W. B. L. Buyers, Consulting Scientist, physicist at the Chalk River Nuclear Research Center in Canada, and then visiting scientist at ORNL, visited in October 1972 for the purpose of advising us on questions of the solid state physics of anisotropy and impurities in connection with iron carbonate.

Dr. J. W. Cable, Consulting Scientist, ORNL, visited in February 1973 to confer on neutron diffraction analysis of magnetic structure.

Dr. H. A. Gersch, Professor of Physics, Georgia Tech, co-chairman on Mr. Altman's thesis committee and consultant on theoretical aspects of thesis problem.

Dr. D. P. Landau, Assistant Professor of Physics, University of Georgia, on Mr. Altman's thesis committee and consultant on Monte Carlo calculations.

V. TRAVEL

S. Spooner	American Crystallography Association Summer Meeting, August 19, 1971 Ames, Iowa	Delivered paper on $MnBr_2 \cdot 4H_2O$
S. Spooner D.E. Wrege	17th Conference on Magnetism and Magnetic Materials, 16-19 November 1971, Chicago, Illinois	Paper delivered on $FeCO_3$
S. Spooner B.R. Livesay R.F. Altman	18th Conference on Magnetism and Magnetic Materials, 28 November - 1 December 1972, Denver, Colorado	Papers delivered on $FeCO_3$ and cobalt films.

VI. INCIDENT REPORT

There were no unusual incidents during the period covered by this project.

Respectfully submitted,

Stephen Spooner
Senior Investigator

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APPENDIX I

MAGNETIC ANISOTROPY OF ORIENTED COBALT FILMS*

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ABSTRACT

Cobalt films exhibiting a six-fold magnetic symmetry have been grown by vacuum deposition onto (111) faces of copper single crystals. Anisotropy energies were determined by Fourier analysis of planar torque curves. Cobalt films of 2750 Å, 820 Å and 2100 Å had cubic anisotropy constants, K_2, of -7.3×10^4 erg/cc, -1.6×10^4 erg/cc and -7.7×10^3 erg/cc respectively. Uniaxial anisotropy was present and the constant, K_u, was approximately equal to 10^4 erg/cc in these films. Alloy films of Co -6% Fe were also grown on (111) copper single crystal faces. These films exhibited uniaxial anisotropy only with $K_u \approx 2 \times 10^4$ erg/cc. In both pure and alloyed cobalt, the uniaxial axis was unrelated to substrate orientation.

INTRODUCTION

The small lattice misfit between copper and f.c.c. cobalt results in conditions suitable for the growth of epitaxial cobalt films on copper single crystal substrates. The preparation conditions favorable for the growth of epitaxial cobalt films on other substrates have been investigated.[1,2,3] Investigations reported by Jesser and Matthews[4] and by Fedorenko and Vincent[5] demonstrated that the lattice misfit between cobalt and copper is accommodated by a network of dislocations which slips into the interface in the early stages of the growth of a cobalt film. As the film thickness increases, there is evidence[2,4,5] that the strain energy activates dislocation processes which convert part of the film material to the more stable h.c.p. phase.

Investigations of the magnetocrystalline anisotropy and other magnetic properties of f.c.c. cobalt films grown by either vacuum deposition or by electrodeposition have been reported[6-11]. The cubic anisotropy constants are generally determined from analysis of data taken from either (100) or (110) films. Since the constant K_2 appears alone in the anisotropy energy expression for a cubic (111) plane,[12] attempts were made to grow cobalt films epitaxially on (111) surfaces of copper single crystals by vacuum deposition. The magnetic anisotropy in the plane of the films was then measured using a torque magnetometer to determine the resulting anisotropy constants.

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EXPERIMENTAL

The copper crystal substrates employed in this work were wafers about 0.5 mm thick having a (111) major surface. The wafers were obtained from 99.999% pure, one inch diameter bulk copper crystal rods sectioned parallel to a (111) plane by spark slicing. The oriented bulk section was placed in a reactor core until an integrated neutron flux of 10^{17}-10^{18} neutrons/cm^2 was accumulated. The fast neutrons served to introduce point defects in the crystal for pinning dislocations and thereby minimize damage during subsequent preparation steps. About two months later it was possible to spark slice the crystal again parallel to the (111) surface obtained earlier using techniques which yielded large area thin wafers of uniform thickness.

The wafers were polished mechanically to remove surface irregularities introduced by spark cutting and then electropolished in a solution of 2/3 orthophosphoric acid with 1/3 water. The wafers were vacuum annealed at about 1000°C for 6 to 8 hours to remove the radiation hardening and mechanical damage. Laue X-Ray patterns were then made on each substrate to index the orientation.

The cobalt films were deposited at a rate of about 10 Å/sec by evaporation using alumina coated tantalum boats in a pressure environment of about 2×10^{-6} Torr. The substrate was oriented normal to the deposition beam in a furnace located about 12 cm from the source. The substrate temperature was held at 300°C for more than 6 hours prior to and during the film deposition. Desired film thicknesses were obtained and evaporation rates were determined using a quartz crystal thickness monitor previously calibrated for the specific geometry used during these evaporations. The films were circular with a diameter of 20 mm. No external magnetic field was applied during evaporation.

The measurements of magnetic anisotropy were made using an automatic torque magnetometer described previously.[13] The (111) surface plane was suspended horizontally in the field of an electromagnetic which rotated about a vertical axis. The rotational speed of the magnet was only 5 degrees/sec so that the substrate eddy current torque would be negligible. The Fourier components of the torque curves were analyzed with the aid of a computer program.

RESULTS

Cobalt films grown on copper crystals under the conditions described above were found to have a magnetic torque component with a six fold symmetry. The magnetic easy axes for this six 6θ term were along the ⟨112⟩ crystallographic directions of the substrate crystal. In addition, a relatively large uniaxial torque component corresponding to anisotropy constants, K_u, on the order of 10^4 erg/cc

was present in all the cobalt films studied but did not appear to have any particular relationship with the crystallographic orientation of the substrates. Three pure cobalt films deposited on (111) surfaces were found to have a measurable sin 6θ component. Several other films deposited under similar conditions did not exhibit a sin 6θ magnetic anisotropy component. However, two of these were deposited at a lower substrate temperature of 200°C indicating that the higher substrate temperature is more favorable for cobalt films having large oriented f.c.c. grains. Cobalt films were also deposited under similar conditions onto polished polycrystalline copper, glass and mica substrates. These films had only a sin 2θ component with K_u in the range of the values obtained for cobalt films deposited on copper single crystal substrates. The source of the uniaxial anisotropy term must therefore have been associated with some factor other than the crystallography of the substrate.

The magnetocrystalline anisotropy constants given here were evaluated in terms of the anisotropy energy expansion for a cubic crystal structure. In most cases, the cobalt films were a mixture of f.c.c. and h.c.p. phases. However, the electron diffraction patterns indicated that the six fold magnetic symmetry probably resulted from f.c.c. epitaxy even though part of the film material became h.c.p. during growth. The magnetic anisotropy expansion for the torque in the (111) plane of a cubic crystal is[12]

$$-\frac{dE_k}{d\theta} = K_2 \frac{\sin 6\theta}{18} \qquad (1)$$

where the torque, L, is $-dE_k/d\theta$ and θ is measured from the [112] direction in the (111) plane.

Planar torque curves made at three applied fields for a 2750 Å cobalt film are shown in Figure 1. The torque curves, both for positive and negative rotations, made at fields of 4000 oersted and above for this film were coincident so that magnetization vector angle corrections were not needed. Fourier analysis of this curve yielded $K_u = 4.1 \times 10^4$ erg/cc and $K_2 = -7.3 \times 10^4$ erg/cc. A very large rotational hysteresis occurred in the neighborhood of 1000 oersted and the low field torque curves were characterized by a rotatable anisotropy in that the phase of the sin θ torque curve obtained at 20 oersted was completely determined by the direction of the last applied high field of 4000 oersted or greater. The back reflection electron diffraction patterns showed that this particular film was a nearly perfect f.c.c. crystal.

For an 820 Å cobalt film the Fourier analysis of the high field torque curves yielded $K_u = 6.2 \times 10^3$ erg/cc and $K_2 = -1.6 \times 10^4$ erg/cc.

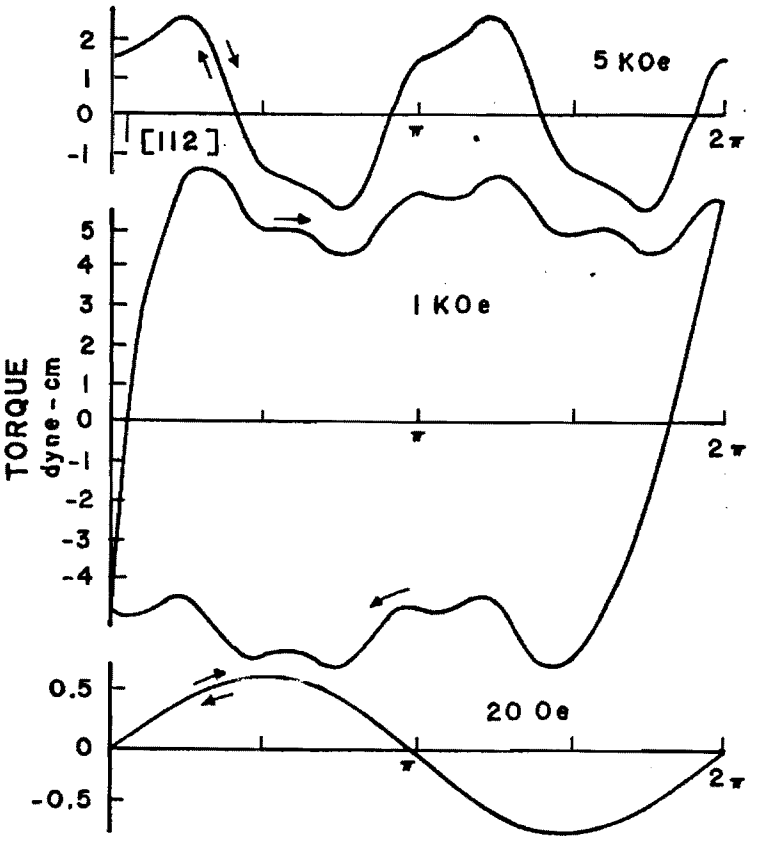

Fig. 1 Torque curves for a 2750 Å f.c.c. cobalt film grown on a (111) copper crystal at the indicated applied fields.

A third film 2100 Å thick had $K_u = 5.2 \times 10^3$ erg/cc and $K_2 = -7.7 \times 10^3$ erg/cc. The back reflection electron diffraction patterns for these films were rings with the f.c.c. reflection spots superimposed. Therefore only part of the film material had the crystallographic orientation of the substrate. It is reasonable to assume that only the oriented f.c.c. material in the cobalt film contributed to the sin 6θ component. No film orientation evidence was detected on any of the electron diffraction patterns for the films which did not have a sin 6θ component.

Additional attempts were made to prepare f.c.c. films which were

primarily cobalt by evaporation from the Co - 6% Fe alloy which has a stable f.c.c. structure at room temperature. This series of films was deposited on (111) copper crystal surfaces using the same deposition parameters which resulted in f.c.c. pure cobalt films. None of these films had a sin 6θ component which could be resolved from the resulting uniaxial torque curves. The values of K_u for the Co - 6% Fe films ranged between 1×10^4 and 5×10^4 erg/cc.

DISCUSSION

The anisotropy constants, K_2, measured for the cobalt films deposited here are somewhat smaller than the values reported by Fisher and Goddard.[10] Their films were electrodeposited onto (110) copper single crystal substrates and the values of K_2 were resolved with K_1. Since bulk cobalt does not exist with an f.c.c. structure at room temperature, no comparisons there were possible. It should be noted that the film having the largest value of K_2 was also the one having greatest crystallographic perfection as seen from the electron diffraction patterns.

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APPENDIX II

APPENDIX III

APPENDIX IV

MAGNETIC LONG RANGE ORDER IN $FeCO_3$*

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ABSTRACT

The sublattice magnetization of $FeCO_3$ has been obtained as a function of temperature from neutron diffraction data. Integrated magnetic Bragg intensities were collected from 4.2K to several degrees above the ordering temperature ($T_N \sim 38$ K). These measurements are compared with the results of Monte Carlo calculations based on an Ising-like S = 1/2 spin model having the $FeCO_3$ structure. Both nearest and next-nearest neighbor interactions are considered in the calculations. When the results of these calculations are normalized to give the observed ordering temperature, it is found that the shape of the measured sublattice magnetization curve can best be fit using an antiferromagnetic nearest neighbor interaction, and a ferromagnetic next-nearest neighbor interaction that is approximately one-quarter as large. These interaction constants are consistant with the interaction constant obtained by combining the Monte Carlo results with measured critical field and ordering temperature values.

INTRODUCTION

Among the carbonates which have the calcite structure, iron carbonate seems to provide a unique example of an antiferromagnetic system with an Ising-like ground state. The highly anisotropic crystal field environment of the iron ions, together with an unquenched orbital angular momentum which couples with the spin of the unpaired 3d electrons in the Fe^{2+} ions are thought to be responsible for this Ising character. The Ising character of the ground state was predicted in a paper by Kanamori, [1] and has since been tentatively experimentally confirmed.[2,3] Although there is some question as to the correctness of Kanamori's ground state description,[4] the results of the sublattice magnetization measurements and calculations reported in this paper add further evidence that the ground state of iron carbonate is Ising-like.

EXPERIMENTAL PROCEDURE

Integrated Bragg intensities were measured from a ground spherical crystal (5.5 mm diam.) of natural iron carbonate (7% by weight impurity content) at the Georgia Tech Neely Nuclear Research

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Center. The crystal was mounted in a cold finger helium cryostat with the 111 and 100 reflections in the scattering plane. Integrated intensities from the 100, 300, and 344 reflections were collected at temperatures from 4.2 K to 41 K. Thermal gradients in the sample were minimized by mounting the crystal inside an aluminum chamber thermally connected to the cold finger. Temperature was controlled by a resistance thermometer attached to the cold finger and the crystal temperature was measured independently by a calibrated germanium thermometer mounted close to the sample. The sample was maintained at each temperature until no drift could be detected in the sample temperature (< 0.1 K) or in the integrated intensity.

A nuclear reflection was measured after each magnetic determination to monitor instrumental drift. As a precaution against possible systematic errors, data were taken over the temperature range in a random order of temperatures and some of the first measurements were repeated at the end of the experiment. The nuclear integrated intensities indicated a variation of $\pm 1.5\%$ while the purely statistical counting error was 0.5%.

The effect of extinction was determined by comparing the intensity versus temperature profiles of the 3 reflections which diffrered greatly in counting rate because of the magnetic form factor. The normalized profiles for these reflections were different, but they could be brought into coincidence by applying an isotropic extinction correction to the measured intensities. The maximum extinction correction in the 003 reflection was 2% and the intensities from this reflection were used for the comparison with the Monte Carlo results.

MONTE CARLO CALCULATION

The behavior of 3 dimensional Ising systems has been studied extensively by a variety of techniques. Some, such as mean field theory, are straightforward but yield quantitatively unreliable results. Others, such as series expansion, are more accurate but are quite unwieldy, particularly when the next-nearest neighbor interactions are considered.

A Monte Carlo procedure described elsewhere,[5] allows an accurate calculation of thermodynamic properties over a wide temperature range. In addition, this Monte Carlo procedure allows one to include in the calculation any energy mechanisms that may be of importance in a real physical system, such as interactions with many different shells of neighbors and contributions from excited energy states.

For reasons discussed later, only first and second nearest neighbor interactions were considered in the present paper. The Hamiltonian was taken to be of the form:

$$H = K_{NN} \sum_{i,j} \sigma_{iz} \sigma_{jz} + K_{NNN} \sum_{i,k} \sigma_{iz} \sigma_{kz}$$

where the sums i,j and i,k are taken over pairs of nearest and next-nearest neighbors respectively (both six in number) and $\sigma_z = \pm 1$.

In order to correct for finite sample size effects we carried out calculations for three different lattice sizes: 4x4x12, 6x6x18 and 8x8x24. Some of our work on other lattices has indicated that bulk properties should vary inversely with the linear dimensions of the sample, viz., the maximum possible correlation length. For this reason we chose all the lattices to be of the same shape so that we could choose any of the linear dimensions of the sample as the extrapolation parameter. It was found that the finite size effects were negligable for $T/T_N < 0.9$. Edge effects were eliminated by applying periodic boundary conditions. The ordering temperature was determined from the inflection point in the energy-temperature data.

COMPARISON OF NEUTRON DATA AND MONTE CARLO RESULTS

In Figure 1, the neutron sublattice magnetization measurements are plotted with the best fitting curve obtained from the Monte Carlo calculations.[6] This curve was obtained for an interaction ratio K_{NNN}/K_{NN} of -0.4. For comparison, the spontaneous magnetization for a Brillouin function for a S = 1/2 model is also shown. (The S = 1/2 model was chosen for comparison because the ground state of Fe^{2+} ion is believed to be an exchange split doublet.) The better agreement gives an indication of the improvement of the Monte Carlo data over the molecular field results. Due to the inaccuracies in the extrapolation technique and statistical fluctuations inherent in the Monte Carlo results, the shape of the sublattice magnetization curve has not been determined exactly (only the smoothed curve is shown). When this uncertainty is taken into account, the agreement between the neutron data and the Monte Carlo curve is reasonably good. However, the neutron data lie consistantly below the calculated curve and it is unlikely that this is a purely statistical effect.

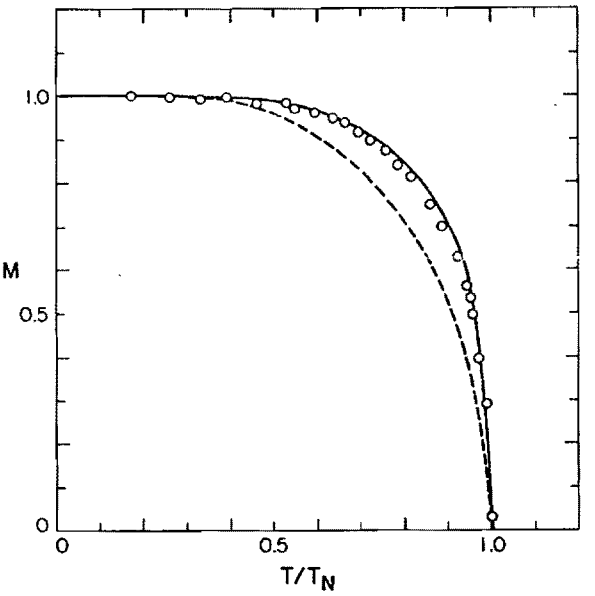

Fig. 1. Sublattice magnetization vs. temperature. Open circles-neutron data: solid line-smoothed Monte Carlo results: dashed line-molecular field curve. Neutron data error limits less than circle size.

There are a number of possibilities for the source of this discrepancy. One is the impurity content of the sample. Another is

that the thermal population of excited states is providing an additional mechanism for lowering the average sublattice magnetization. Although one of the crystal field levels of $FeCO_3$ has been measured,[7,8] a consistant scheme for the entire level structure has not been confirmed, and so no attempt was made in these first calculations to account for the effects of excited states. An estimate of the dipole-dipole interactions for more distant neighbors indicates they are almost two orders of magnitude smaller than the exchange interactions and so it is unlikely that their inclusion would alter our results significantly.

The Monte Carlo results can be combined with recent critical magnetic field and magnetization measurements[2] to estimate K_{NN} and K_{NNN} in another way. The magnetic measurements can be used to determine K_{NN} directly since only the shell of nearest neighbors is turned over with respect to the central ion by application of a magnetic field along the spin direction (the second nearest neighbors lie in a ferromagnetic plane with the central ion). Using the low temperature critical field and magnetization values of 145 KOe and 4.6 μ_B per Fe^{2+} ion respectively, K_{NN} has a value of +7.3K. When K_{NN} is fixed at this value and K_{NNN} is varied, T_N resulting from the Monte Carlo calculation is found to vary in the way shown in Figure 2. This graph shows that $K_{NNN}/K_{NN} = -0.2$ will give the observed ordering temperature of 38.5K. This number is an average of ordering temperatures reported in the literature for better specimens. (The ordering temperature of the sample used in the neutron diffraction study was measured to be 38.0K ±0.3K.) Since no allowance has been made for errors in the magnetic parameters used to calculate K_{NN}, the ratio of -.2 is in reasonable agreement with the neutron value of -.4.

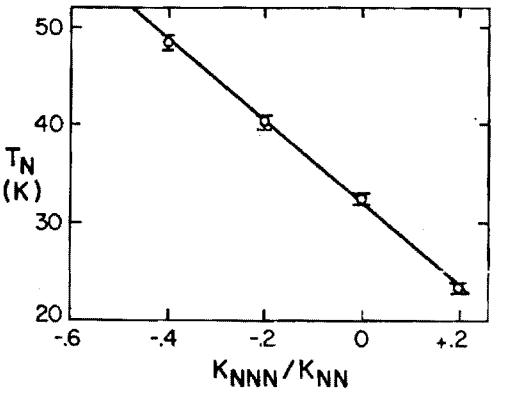

Fig. 2. Dependence of ordering temperature on ratio of next-nearest to nearest neighbor constants. K_{NN} is fixed at 7.3 K.

CONCLUSIONS

It is clear that further work remains to be done. When the properties of the low lying states of the Fe^{2+} ion have been unambiguously determined, these states will be included in the Monte Carlo calculations to see what effect they have on the sublattice magnetization and ordering temperature. Other properties, such as the susceptibility remain to be calculated, and the effects of the impurities need to be accounted for. However, the results for the neutron sublattice magnetization measurements indicate that the ground state of the Fe^{2+} ion in $FeCO_3$ is reasonably well described by a three dimensional, S = 1/2, Ising model with a ferromagnetic

next nearest neighbor interaction that is about one-fourth of the nearest neighbor interaction. The comparison of the Monte Carlo results with the neutron data indicates that this technique represents a significant improvement over the techniques employed in molecular field approximations.

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