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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

MAGNETIC PROPERTIES OF INSULATORS

(Contract No. AT(11-1)-578)
Project Agreement No. 9

Jordan J. Markham

U. S. Atomic Energy Commission
Argonne, Illinois

"AEC Research and Development Report"

25 years of research

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ARMOUR RESEARCH FOUNDATION
of
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

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to

U. S. Atomic Energy Commission
Chicago Operations Office
9800 South Cass Avenue
Argonne, Illinois

Attention: Fred C. Mattmueller
Acting Director
Contracts Division

(Covering the Period from February 15, 1961 to May 15, 1961

May 29, 1961

MAGNETIC PROPERTIES OF INSULATORS

I. INTRODUCTION

The magnetic properties of color centers are of interest because they are one of the principal sources of information regarding electron traps in insulators. The electron paramagnetic resonance is very much affected by interaction of the center with its surroundings as is the optical absorption. A study of the relaxation phenomena of the resonance must consider the transfer of energy between the spin systems and the lattice. The imperfections are at different local fields depending on the orientation of the nuclear spins which surround the trapped electron. The centers are far enough apart that the energy transfers among spins are slow and the principle interactions are with the host lattice. The thermal effects related to the vibration of the ions may be caused by vibrations characteristic of the center itself or the environment characterized by the lattice. We assume these are the principal interactions determining the spin lattice relaxation time.

The spin lattice relaxation time is a property of the F-center which can be used to measure the interaction of the color center electron with certain types of vibrations in the surroundings. The nature of the inhomogeneously broadened line is such that one may saturate a portion of the line without affecting the rest. The recovery rate can be observed directly at liquid helium temperatures. It depends on temperature and concentration. The first set of experiments is designed to determine the equation governing the recovery of the resonance after saturation. This will then be compared with theories on magnetic resonance relaxation. The experimental equipment has been designed and is described in this report.

Previous experiments on inhomogeneously saturated lines have been analyzed in preparation for publishing a paper, and it is shown that there is a possibility that effects of spin diffusion may be observed even at room temperature. A meaningful comparison of experimental results with models and quantitative calculations of the interactions are required. Therefore, work is also being initiated on the theory of lattice vibrations.

The experimental work was conducted by Dr. Gordon Noble with the assistance of Mr. David Brandon. Dr. Noble is responsible for the taking of very careful data on the saturation properties of "pure" and bleached F-centers as well as a careful analysis of the results.

The theoretical work is being carried out by Mr. Thomas Casselman under the general guidance of the Principal Investigator.

II. EXPERIMENTAL

A. Sample Preparation

The relaxation time at 4°K depends on concentration, so crystals with a uniform distribution are required. Relatively large samples are prepared by the method of additive coloration and this equipment has been built and put into operation. The alkali halide crystal is held at the top of a stainless steel cylinder closed by a vacuum tight plug. After the alkali halide crystal and metal are put into the cylinder, it is evacuated in a special pumping unit which allows the plug to be inserted. The cylinder is placed in a furnace with high temperature and low temperature regions. The potassium temperature controls the final concentration and the crystal temperature controls the rate of coloration. After several hours, the crystal is quickly removed from the cylinder using a plug puller and quenched rapidly in oil to obtain all the excess electrons as F-centers. After the equipment for the above process was built, several colorations of potassium chloride were made, and we now have confidence in our procedure and apparatus. Following this, crystals of rubidium chloride were obtained from semi-elements and colored with potassium metal. We find the stress in these crystals is much greater than the KCl from Harshaw. The stress reduces the probability that one can obtain a piece satisfactory for optical absorption measurements, although these smaller pieces may be used for magnetic resonance. It seems that the stress is introduced by the additive coloration process and our procedure is being modified to reduce the stress without introducing other centers.

B. Inhomogeneous Saturation

The inhomogeneously broadened line is common in magnetic resonance. This type of broadening is produced by those interactions with the electron spin which are different for each spin or absorbing center. The total absorption is the sum of the many different absorption curves. Although direct measurement of the width and relaxation time of the individual centers is prevented by the averaging process, the saturation of the resonance depends upon these factors and the distribution characteristic of the centers. Color centers in solids have been very suitable for investigation of these effects. The magnetic resonance of the F-center was the first illustration of the inhomogeneously broadened line. Kip, Kittel, Levy and Portis [1] showed that the width of the magnetic resonance absorption was caused by the hyperfine coupling with the nuclei surrounding the center. Portis[2] studied the saturation of the F-center resonance and showed that it could be described using simple assumptions. The resonance of the individual center, called the spin multiplet, was assumed narrow compared with the width of the distribution of multiplets caused by the hyperfine interaction. The shape of the multiplet was assumed Lorentzian as a function of the magnetic field.

In earlier work, we have investigated the resonance of the "pure" F-center. The experimental work was done at the Zenith Radio laboratories; the analysis of the data was done at A.R.F. on the contract. In view of the number of measurements, this was a lengthy task. If the saturation can be described by the simple relationship derived by Portis, a parameter may be obtained which depends on the width of the individual multiplet. This width originally was assumed to be caused by the electron dipole interaction between F-centers, i.e., it would be concentration dependent. We have investigated the saturation as a function of concentration and find no significant dependence. The data fit the simple saturation relationship only below a critical power level. Above this power, there is a departure from the equation. A similar high power behavior has been observed by Silsbee[3] at room temperature. Our data include measurements of the unsaturated susceptibility at liquid nitrogen and liquid helium temperatures. One may consider why this has not been observed earlier. It may be related to the detection systems used or the portion of the line which is observed. The present measurements are over a wider power range.

Castner[4] has discussed the saturation of the V_k center which is also inhomogeneously broadened. He observes an effect similar to the one we observe for the F-center. However, the theory he derives explains this behavior by attributing it to multiplets which, although Lorentzian, are comparable in width to the inhomogeneous line. Our line shape and width do not change. It can be shown that a departure from Lorentzian shape caused by including a fourth power of frequency will produce the change in slope, although the multiplet is narrow compared to overall line width. The resonance of F-centers in potassium iodide[5] fits the simple equation, so it would seem that the extremely long relaxation time in KCl might allow a different relaxation mechanism to take over above a critical power.

C. Application to the Bleached Crystals

The bleaching of the F-center to form the B-band produces a different resonance. The g factor remains the same but the width decreases from 45 to 35 gauss. The width and line shape do not change as the line saturates. This indicates that the line is inhomogeneously broadened. However, the saturation increases much more slowly as the power increases, than the saturation of the F-center. Qualitative considerations indicate that the shape of the multiplet has changed so that a greater portion of the area of the mulbiplet is in the tail where saturation is less.

Further investigation of the inhomogeneous broadening is being carried on in order to find a theory which can explain the resonance in the bleached crystals. The details of this discussion will be presented at a later time in a preprint of a paper.

D. Measurement of T_1 at 4°K

The equipment for study of the relaxation phenomena in F-centers has begun by developing improved equipment for observing the saturation and recovery of a portion of the resonance at 4°K. A conventional spectrometer will be used for the magnetic field, microwave generator and signal frequency stabilization circuits. A magic tee bridge will be used for coupling to the reflection cavity which resonates in a rectangular TE_{011} mode and has been designed for use at liquid helium temperature. Because of the very low powers which are associated with the long relaxation times, the microwave power will be detected by a superheterodyne system.

The unique feature of these experiments is the magnetic field modulation. Continuous observation of the magnetic resonance even at these low power levels will cause saturation when the relaxation times are long. The relaxation should occur when the spins are not interacting with the electromagnetic field in the cavity. The requirement is that most of the time the spins are not in resonance and that periodically the resonance is observed to measure its recovery. The initial power level used for saturation is important since there is evidence from previous experiments[6] that the relaxation time may depend upon the fractional saturation. Considering these factors, the magnetic field modulation equipment has been designed to give the time dependence shown in Fig. 1. The equipment built and tested for this is outlined in Fig. 2. It allows wide variations in the times important to the experiment. T_s, the time during which saturation occurs, is very long compared to the relaxation time and allows the system to come to equilibrium with the applied power. T_d is a delay time which occurs between the end of saturation and the beginning of the first passage through the resonance. It is important for determining the rate law of the recovery that the first observation be made soon after saturation. T_r is repetition period between observations of the resonance. The system shuts off after a few traces of the resonance to prevent interpretation difficulties caused by too many overlapping lines in the photograph.

Special field modulation coild have been designed and built for this system. The field produced by a set of coils properly matched to a generator is proportional to the power input and the volume available for the coils. In the geometry for the experiment, the large sweeps and homogeneous fields are not compatible. Therefore, two sets of coils have been designed and built.

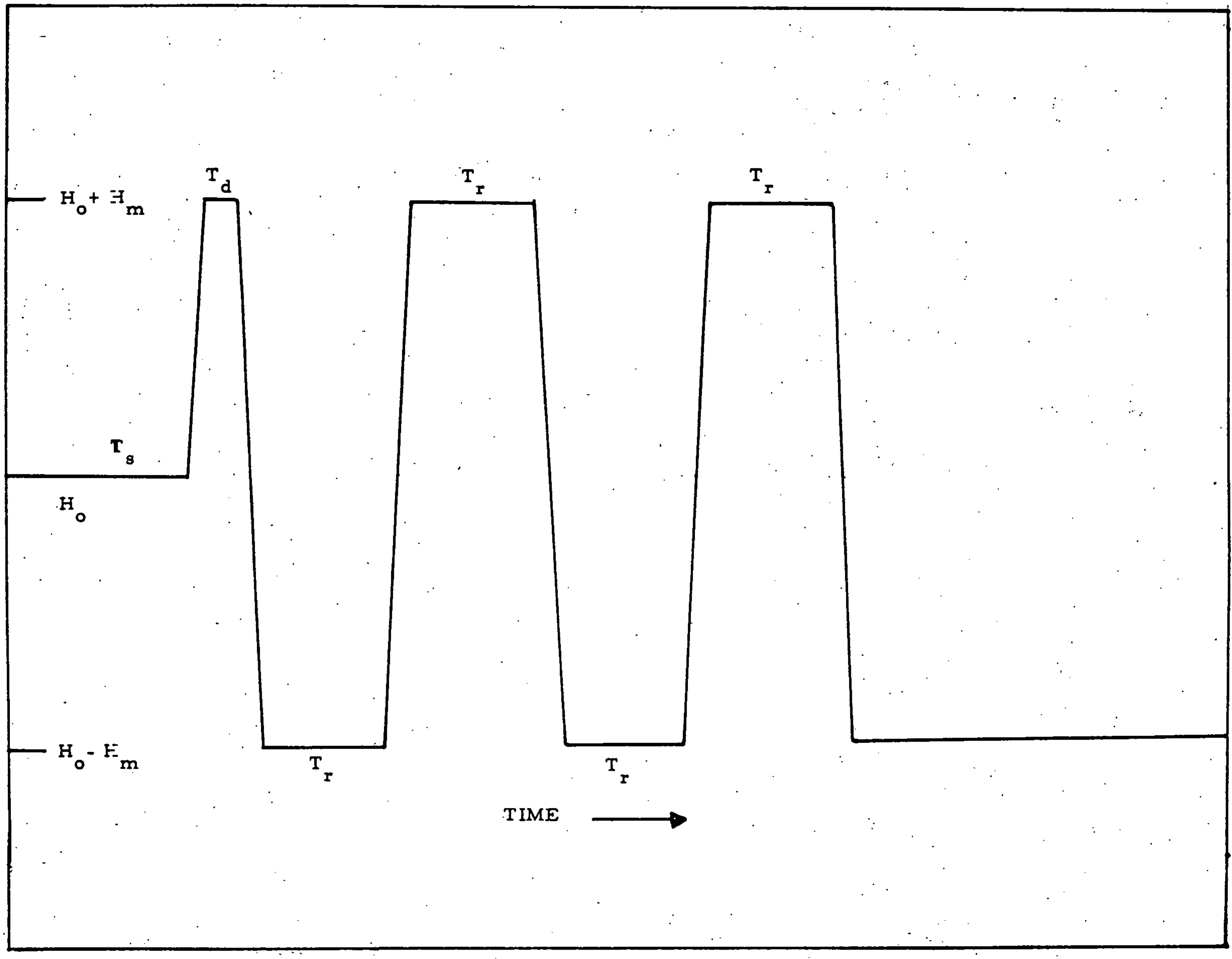

Fig. 1

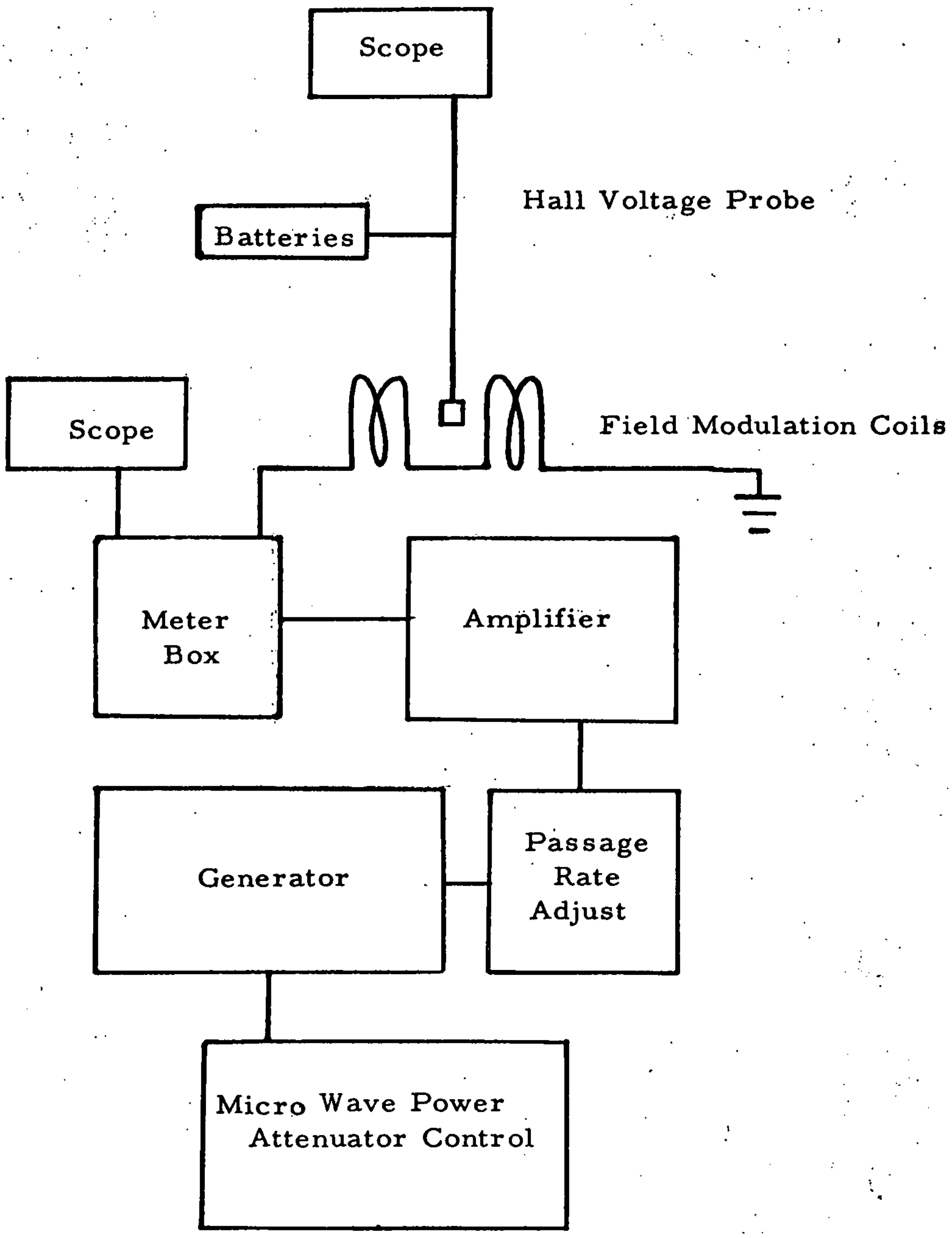
Scope
Hall Voltage Probe
Batteries
Scope
Field Modulation Coils
Meter Box
Amplifier
Generator
Passage Rate Adjust
Micro Wave Power Attenuator Control

Fig. 2

The small coils producing a very homogeneous magnetic field have low heat dissipation and are restricted to small modulation of very short duty periods. The larger coils can provide large modulation for long periods but the field gradient is about a gauss over an inch occupied by the sample.

III. THEORETICAL

In line with the stated objective of our research, we have started to explore the interaction between the vibration of the ions around a negative-ion vacancy in an alkali halide and an electron trapped at that site (the F-center).

A great many types of lattice vibrations exist. Some of these are: (1) longitudinal optical modes; (2) transverse optical modes; (3) longitudinal acoustical modes; (4) transverse acoustical modes and (5) local modes which concentrate their displacement around point imperfections. Some of these modes do not affect the trapped electron to a measurable extent while others create a time dependent scalar and a vector potential which strongly interacts with the electron. Our overall objective is to understand the form of these interactions and to formulate them in an explicit manner. The vector potential is produced by transverse or the quasi transverse optical modes and causes the spin lattice relaxation process. The longitudinal optical modes contribute to the scalar potential which causes the interactions between the ions and the charge of the electron and manifests itself in the broadening of the absorption and emission bands of the center.

In recent years, three important contributions to this problem have been made. The first due to Bjork and Krumhansl[7] concerns itself with the local modes. They indicate that around an imperfection, the largest mode is most probably of the type 5 whose amplitude is damped as the distance from the imperfection increases. Their arguments were explicitly carried out for a diatomic chain with a point imperfection at the very center. It employs some extremely general mathematical theorems; hence their results are not limited to a particular model and certainly apply to point imperfections in real lattices. Unfortunately, the Bjork-Krumhansl formulation does not include the effects of temperature and actually, it is not complete.

Two recent calculations have been made by Rosenstock and Klick[8] as well as by Karo, McCombie and Murray.[9] The first paper suggests that the broadening of the F absorption band may come from the lattice modes. The second calculation uses a more explicit model and indicates that the crystal modes lead to the wrong effective frequency; they suggest that local modes should be considered in detail. In their calculations, Rosenstock and Klick use the correct formulation of the Bjork-Krumhansl theorem, although they do not formulate it explicitly or show how it can be employed in actual crystals.

We have re-examined and reformulated the Bjork-Krumhansl theorem introducing the normal modes explicitly and showing the effects of temperature and frequencies of the modes. We believe this is extremely important when one generalizes theorems arising from simple models so that they can be applied to actual crystals. The results show that at low temperature, the high frequency modes contribute less than would have been expected from the formulation given by Bjork.

Our new formulation gives us a handle to discuss the problem of actual crystals and a feeling for the problems involved. Another point has been made regarding the parity (even and odd) of modes of the lattices. It is our feeling that these problems arise because of an unusual geometry which has assumed, namely, that the ends of the chain are stationary and that the imperfection is at the very center of the lattice. If we should change the boundary condition or if we employ the Born-von Karman conditions, this parity law does not seem to arise and, therefore, it may not be an essential property of real lattices. This problem must be studied further.

Some theoretical time has been spent by Thomas Casselman in the study of the general theory of F-centers in alkali halides in preparation for further work.

IV. WORK PLANNED FOR NEXT QUARTER

In the next quarter, we expect to begin obtaining data on T_1 at 4°K. We will also continue the theoretical calculations on the electron interactions with phonons. Some effort will continue on the theory of inhomogeneous broadening in order to interpret the departure observed from the simplest saturation relationship and use this to measure quantities of interest at higher temperatures.

Respectfully submitted,

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