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NAVORD REPORT 2859

PROGRESS REPORT OF THE SOLID STATE DIVISION  
FOR CALENDAR YEAR 1952 (PART I)

22 MAY 1953



**U. S. NAVAL ORDNANCE LABORATORY**  
**WHITE OAK, MARYLAND**

PROGRESS REPORT OF THE SOLID STATE DIVISION  
FOR CALENDAR YEAR 1952 (PART I)

Prepared by:

Louis R. Maxwell

FOREWORD: This is the second annual progress report of the Solid State Division and is a more comprehensive treatment of the activities for 1952 than was presented in our first annual report which limited its scope to those problems which were considered the most outstanding. We present here a reference to every unclassified problem that reached the completion stage during 1952 although the work may not have been published within this period. The reader will be aware of the scope of the Solid State Division and its degree of coordination working towards common goals. Work done for other departments within the Naval Ordnance Laboratory, referred to as services, rounds out the description of our activities. We are indebted to the U. S. Office of Naval Research for financial help and continued encouragement throughout the year.

U. S. NAVAL ORDNANCE LABORATORY  
WHITE OAK, MARYLAND

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PROGRESS REPORT OF THE SOLID STATE DIVISION  
FOR CALENDAR YEAR 1952 (PART I)

INTRODUCTION

1. During 1952 the Solid State Division (formerly known as the Solid State and Optics Research Division) enjoyed its first year of research as a unit free of major reorganizations. Although the name of the Division was shortened, the objective and research programs were unaffected. After having served as Division Chief throughout the major portion of the year, Dr. D. F. Bleil moved to Deputy Chief of the Physics Research Department in September 1952, and Dr. L. R. Maxwell returned as Division Chief--no other major changes in personnel were made.
2. An objective of the Solid State Division is to obtain a better understanding of solids. We are undertaking this problem through a study of the kinetics of holes and electrons in semiconductors; the investigation of the interaction between magnetic ions or atoms in oxides and metals; and by the study of the interaction of electromagnetic radiation with magnetic, electronic, and ionic systems. With these objectives we undertake our explorations through those channels that appear to be most fruitful and ones that can be followed most expeditiously.
3. We are also concerned with military problems pertaining to the use of electromagnetic radiation, whose spectrum lies in the region from the ultraviolet to the far infrared.
4. Because of the nature of our basic programs, we are able to support and carry out special research problems to be used by certain employees as partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Maryland or Catholic University. During the year 1952 we employed four men under such an arrangement; one of them completed his requirements by a satisfactory experimental study of a phase of our magnetic program. At the end of the year we carried three problems in this status, one on the phenomenon of electroluminescence, one on the Hall effect in thin films of photoconductors, and one on photoconductivity in lead selenide.

MAGNETISM IN SOLIDS

Molecular Field Treatment of Ferromagnetism and Antiferromagnetism

5. Insight into the nature of both ferro and antiferromagnetism can be gained by a study of the variation of the molar

susceptibility ( $\chi$ ) with temperature. This relationship can be expressed by

$$\chi = C_M / (T - \theta) \quad (1)$$

where  $C_M$  is the molar Curie constant,  $T$  is the absolute temperature, and  $\theta$  is a constant that depends on the nature of the material. The value of  $\theta$  plays an important role in the understanding of the type of molecular fields present. If  $\theta$  is positive, for example, we see from equation (1) that the molar susceptibility is greater than would be obtained from the value of  $C_M/T$ , the situation existing for a gas. We interpret this to show that above the Curie temperature the internal fields favor ferromagnetism or favor a cooperative parallel alignment of magnetic spins. If, on the other hand,  $\theta$  is negative, then our molar susceptibility is less than  $C_M/T$ , indicating that the internal field hinders the applied field and tries to maintain the spin orientations in opposition or towards antiferromagnetism. The Curie temperature ( $T_c$ ) is dependent on the type of ordering that occurs while  $\theta$  is independent of the ordering. The quantity  $kT_c$  is a measure of the energy required to go from a state of perfect order to one where the magnetic order is destroyed.

6. In the simplest approximation  $\theta = \pm T_c$ . Departures from the ideal case afford an opportunity to learn more about the nature of the molecular fields coupling the magnetic ions together. The approach described above has been made by Smart<sup>12</sup> who has calculated  $\gamma_2/\gamma_1$ , the ratio of the Weiss field coefficients for second and first nearest neighbor interactions, for the known values of  $\theta/T_c$ .  $\gamma_2/\gamma_1$  can be uniquely determined when the type of ordering is known. In most instances, this information has been obtained from neutron diffraction studies. Smart has shown that in some materials  $\gamma_2/\gamma_1$  is less than one, which means that the first nearest neighbor<sup>1</sup> interaction predominates; an example is the case of  $MnF_2$  where  $\gamma_2/\gamma_1 = 0.22$ ; the first nearest neighbor interaction is about 5 times as strong as the second nearest neighbor interaction. In the case of  $FeO$ , however, the second nearest neighbor interaction is about 1.6 times that of the first nearest neighbor interaction ( $\gamma_2/\gamma_1 = 1.57$ ).

### Magnetic Structure Transitions

7. Smart has been able to show that there are critical values for the molecular field coefficients for interaction between nearest and next-nearest neighbors, such that at certain temperatures one might find transitions involving a change in magnetic ordering. An example is the case of  $MnAs$  where a transition from ferromagnetic to antiferromagnetic arrangement

occurs. This type of transition can be studied using thermodynamic considerations. Smart introduced an additional refinement whereby he assumed that the molecular field coefficients depended upon the temperature in a linear fashion as:

$$\gamma = \gamma_0(1 + \alpha T) \quad (2)$$

By considering the temperature variation of the molecular field coefficients, the theory showed that at certain temperatures first order transitions should occur as observed.

8. Crystal structure changes that take place when an antiferromagnetic material is cooled from its paramagnetic to its antiferromagnetic state can be determined accurately by means of a symmetrical back-reflection x-ray diffraction camera. CoO and MnTe were investigated in this manner by Selma Greenwald. She found for cobalt monoxide that below the transition temperature the structure became tetragonal with an increase in the "a" axes and a decrease in the "c" axis but in such a way that the volume decreased linearly with temperature. This deformation was not expected since neutron diffraction experiments indicate that alternating (111) planes have opposite spins. If one assumes that there is an interaction between atoms with unlike spins, then the deformation should be perpendicular to the (111) planes giving a rhombohedral rather than a tetragonal deformation. This anomaly has not yet been explained.

9. In the case of manganese telluride no change in symmetry was observed at the transition temperature; however, the "c" axis dropped abruptly below the Curie temperature while the "a" axes decreased in a linear fashion corresponding to an ordinary temperature contraction. From this data Greenwald concluded that the magnetic ordering should be such that the (0001) layers should have alternating spins. Such an ordering would be especially favorable for nearest and third nearest neighbor antiferromagnetic interaction.

#### Magnetic Susceptibility of Solids

10. Investigation of nonferromagnetic transition elements affords a method for studying the exchange interaction between electrons in the d shells. The Heisenberg theory postulates a negative interaction between the d shells, particularly for chromium and manganese; Néel and Zener both conclude that the nonferromagnetic transition elements should be antiferromagnetic.

11. The variation of magnetic susceptibility with temperature is an effective way to study the nature of these interactions. McGuire and Kriessman<sup>7</sup> have measured the magnetic susceptibility of chromium from -195°C to 1440°C and found that the susceptibility increases with temperature as an antiferromagnetic material should behave, but they found no break in the

susceptibility as would occur at a Curie temperature. In the neighborhood of 1400°C a susceptibility temperature hysteresis loop was found that indicated either a change in phase or a secondary effect due to  $\text{Cr}_2\text{O}_3$  present as an impurity.

12. Other metals belonging to this transition group are vanadium, niobium, tantalum, tungsten, and molybdenum. The variation of the magnetic susceptibility of these elements with respect to temperature provides information concerning the energy states of the conduction electrons. A general study of the magnetic susceptibility of these elements was made by C. J. Kriessman. He found that vanadium, niobium, and tantalum show a decrease in magnetic susceptibility with temperature while molybdenum and tungsten show an increase in susceptibility with temperature. An approach to an explanation of this phenomena was made by considering the collective electron picture proposed by Stoner which is expressed as follows:

$$\chi = \chi_0 (1 + C\chi T^2); \quad \chi = \left[ \frac{\partial^2 \ln N(E)}{\partial^2 E} \right]_{E_0} \quad (3)$$

where  $N(E)$  is the number of energy states per energy interval,  $\chi_0$  and  $C$  are constants. The sign of the temperature coefficient  $\chi$  depends upon the shape of the curve representing the energy density of conduction electrons. Since the Fermi energy ( $E_0$ ) may lie close to a minimum in  $N(E)$ , a positive coefficient may be expected as found for certain elements. Kriessman, moreover, has shown that when the susceptibility data is collected for all of the transition elements, the sign of the coefficient varies alternately according to the column of the periodical table in which the element lies.

### The Chromites

13. By replacing the trivalent iron ion in the ferrites by trivalent chromium, a series of materials known as the chromites were prepared. They are identified as  $X\text{O} \cdot \text{Cr}_2\text{O}_3$  where  $X$  is one of the following: Zn, Mg, Mn, Fe, Ni, Co, or Cu. These materials, by x-ray analysis, were found to have the spinel structure with the exception of copper chromite which was tetragonal. McGuire, Howard, and Smart<sup>20</sup> measured the magnetic susceptibility of these materials as a function of the temperature. In the case of zinc and magnesium chromite, they found negative values for  $\theta$  indicating negative exchange interaction between the chromium ions. When the nonmagnetic divalent ions are replaced by magnetic ions, such as nickel and manganese, a ferrimagnetic behavior is found with Curie temperatures between 40 and 50°K.

14. Cobalt chromite and copper chromite which have Curie temperatures above liquid nitrogen showed a variation of



susceptibility with temperature in agreement with the Néel theory. The saturation magnetization determined below the Curie temperature indicated that the saturation moment was 0.4 Bohr magnetons per molecule for copper chromite. In the case of cobalt chromite a saturation moment of 0.1 Bohr magnetons per molecule was observed. These values are considerably lower than one would expect on comparison with the same divalent substitution in the ferrites.

### Ferroxcube III

15. Ferroxcube III is a commercial name for a zinc manganese ferrite. It was of interest to examine the variation of a-c permeability of such material with frequency and with temperature. Talbert<sup>1</sup> found that the a-c permeability was independent of frequency up to 200 kc. Variations of permeability were obtained by applying a strong external magnetic field. As the field increased, the permeability decreased by a factor of over 300. It was also found that the permeability changed rapidly in the vicinity of the Curie temperature which is approximately 150°C. The loss also increased as the permeability decreased rapidly. These variations of permeability are important for practical applications to tuned circuits.

### Antiferromagnetic Resonance

16. Electronic magnetic resonance involves a coupling between an applied high frequency microwave field and uncompensated electron spins that experience certain precessional motions under the influence of a steady external magnetic field. When the frequency of the applied field equals a normal frequency of precession, resonance magnetic absorption occurs. This problem was investigated both experimentally and theoretically.

17. Experiments by Maxwell and McGuire extended previous work which had showed that the amount of absorption at resonance decreased to only a small residual as antiferromagnetic materials were cooled through their Curie temperatures. The rate at which the absorption decreased varied with the material; for  $\text{Cr}_2\text{O}_3$  the drop was very sharp, while for  $\text{MnO}$  it occurred more gradually. In the case of manganese selenide, an absorption vs. temperature hysteresis loop was observed that was correlated with a similar loop observed in susceptibility measurements. The experimental results for all of the antiferromagnetic materials studied show that, at the frequencies used, there was no appreciable resonance absorption below the Curie temperature, indicating that resonance as observed in ferromagnetic materials does not occur. Figure 1 shows a photograph of the apparatus used.

18. A better understanding of this phenomenon was obtained by Wangness<sup>11</sup> from a general treatment of magnetic resonance in

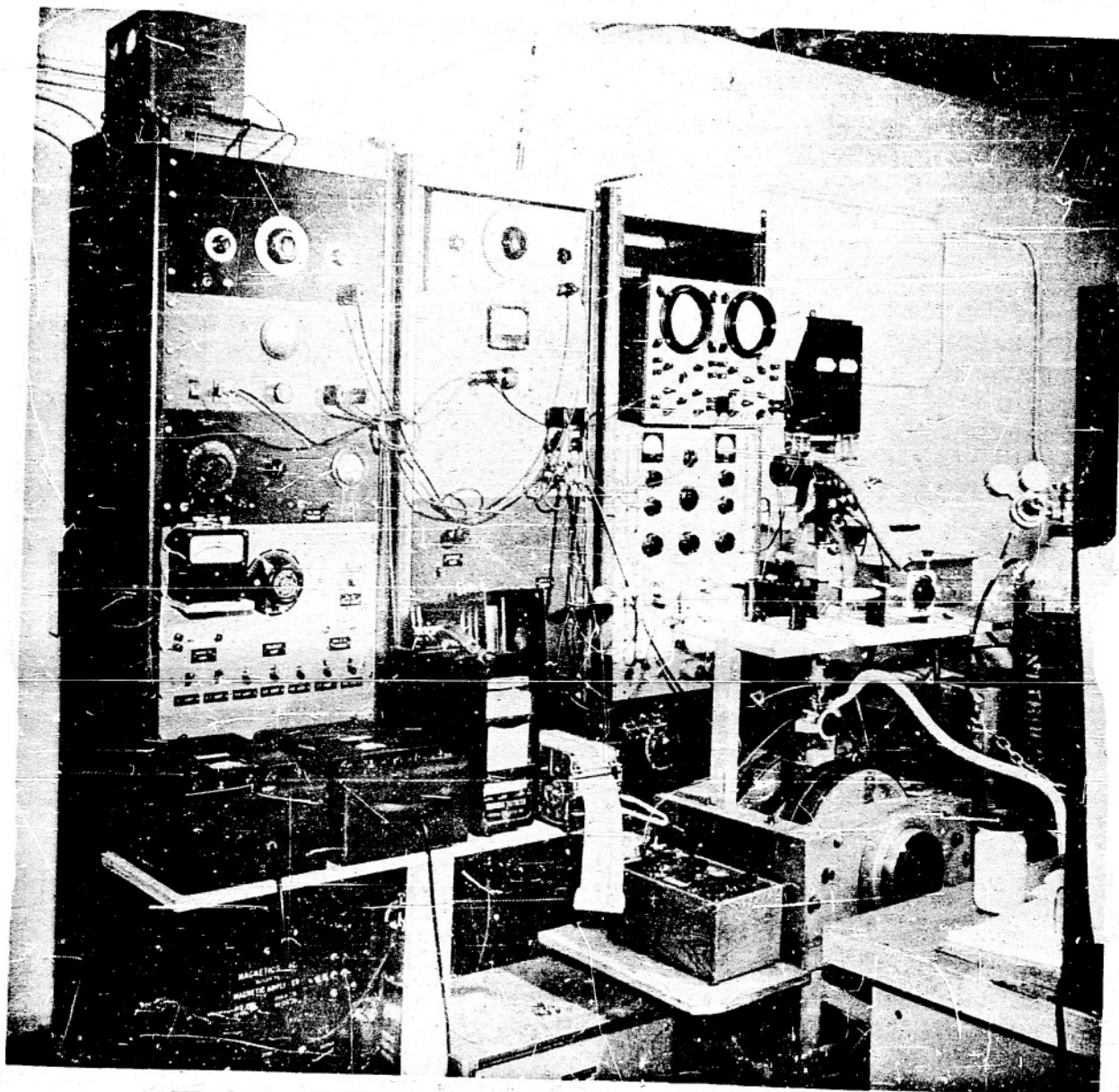


FIG. 1 EQUIPMENT USED FOR ELECTRONIC  
AND MAGNETIC RESONANCE.

a system containing two magnetic sublattices. He was able to show that the normal frequencies of precession in an antiferromagnetic material lie well beyond the region investigated experimentally, i.e., to much higher frequencies; his interpretation is a more general treatment of a previous calculation made by Kittel. Wangsness also predicted that in a ferromagnetic system there should exist normal frequencies out in the far infrared.

19. The way in which the absorption in an antiferromagnetic material decreases with temperature has been explained by Wangsness from a consideration of short range ordering. A qualitative agreement between experiment and theory was obtained for MnO.

20. We now understand, in our resonance investigations of antiferromagnetic materials, why the absorption is so weak at the frequencies and temperatures investigated and why the absorption decreases as it does when the material is cooled from its paramagnetic state to the Curie temperature. Many other problems, such as the question of relaxation times, quantitative determination of the amount of absorption, and more details as to the agreement between experiment and theory at the point of resonance remain unsolved for further study.

#### Exchange Coupling in Biradicals

21. In certain instances one may have two separated uncompensated electron spins existing within a single molecule such as in an organic biradical where the exchange coupling between the two electrons becomes important. Wangsness<sup>15</sup> has examined this case and he derived a Curie-Weiss law for the high temperature magnetic susceptibility. Such a variation of susceptibility with temperature has been found in some organic molecules.

#### A Heat Capacity Anomaly

22. A quantitative determination of the magnitude of a sudden change in the heat capacity of a substance may lead to important conclusions as to structure changes. Such a situation arose in connection with the anomaly in the heat capacity of MnO in the region from 100 to 122°K. Wangsness<sup>17</sup> pointed up the fact that after one took into account the absorption of energy by lattice oscillations and the disappearance of spontaneous magnetization there still remained about 48 calories per mole that were unaccounted for.

23. By studying the ratio of  $-Q/T_C$  obtained from the Curie-Weiss law, Wangsness indicated that the excess heat could be due to a change in the antiferromagnetic ordering from a second to a third kind.

## ELECTRICAL BEHAVIOR OF SEMICONDUCTORS

24. Lead sulfide, lead selenide, and lead telluride are a class of compounds that afford opportunities for the determination of the electrical behavior of semiconductors. We believe that a thorough and intensive investigation of these compounds through a study of the Hall effect resistivity and transition effects will lead to important facts of not only general interest in the field of semiconductors, but also with respect to specific applied problems of interest to this Laboratory. See Figure 2 for photograph of single crystals prepared in this program. See Figure 4 for setup used in studying the Hall effect of semiconductors. Sulfur, selenium, and tellurium, appearing in equivalent positions in the sixth column of the periodic table, combine with lead in such a manner as to give a series of solid solutions that will provide important correlations between the type of solution and the electrical properties.

### Capacitance Coupling in Thin Conducting Films

25. Thin conducting films are composed of micro-crystals in contact with each other in such a way as to build up a continuous film. The impedance of these films has been studied as a function of frequency and temperature in an effort to determine the nature of the capacitive coupling between various crystallites. Such investigations have been made by Humphrey, Lummis, and Scanlon<sup>4</sup> for thin films of lead sulfide and tellurium. They were concerned with the problem of distinguishing between inter-crystalline and distributed capacitances. The intercrystalline capacitance comes as a result of the capacitance between crystallite faces, while the distributed capacitance can be considered as due to the capacitance existing between various parts of the film symmetrically located with respect to each other. The distributed capacitance gives rise to a nonuniform distribution of charge lengthwise of the material when there is a current flow.

26. An effort was made to distinguish between the two concepts mentioned above for the films studied. It turned out that there was no general distinction between the two; but, rather, for some films their behavior indicated both distributed and inter-crystallite capacitance, while for others the distributed capacitance alone was sufficient to explain the experimental results. Furthermore, Humphrey, Lummis, and Scanlon showed that photo-conductivity exists either with or without measurable inter-crystallite capacitance effects.

### Response Time in Semiconductors

27. The nature of the response time in semiconductors provides a suitable means for an understanding of the mechanisms of



FIG. 2 SINGLE CRYSTALS OF LEAD SELENIDE GROWN BY DR. ROBERT F. BREBRICK



FIG. 3 EQUIPMENT ARRANGED TO STUDY PHOTO-  
CONDUCTIVITY, CONTACT RESISTANCE AND  
TRANSISTOR EFFECT IN SEMICONDUCTORS



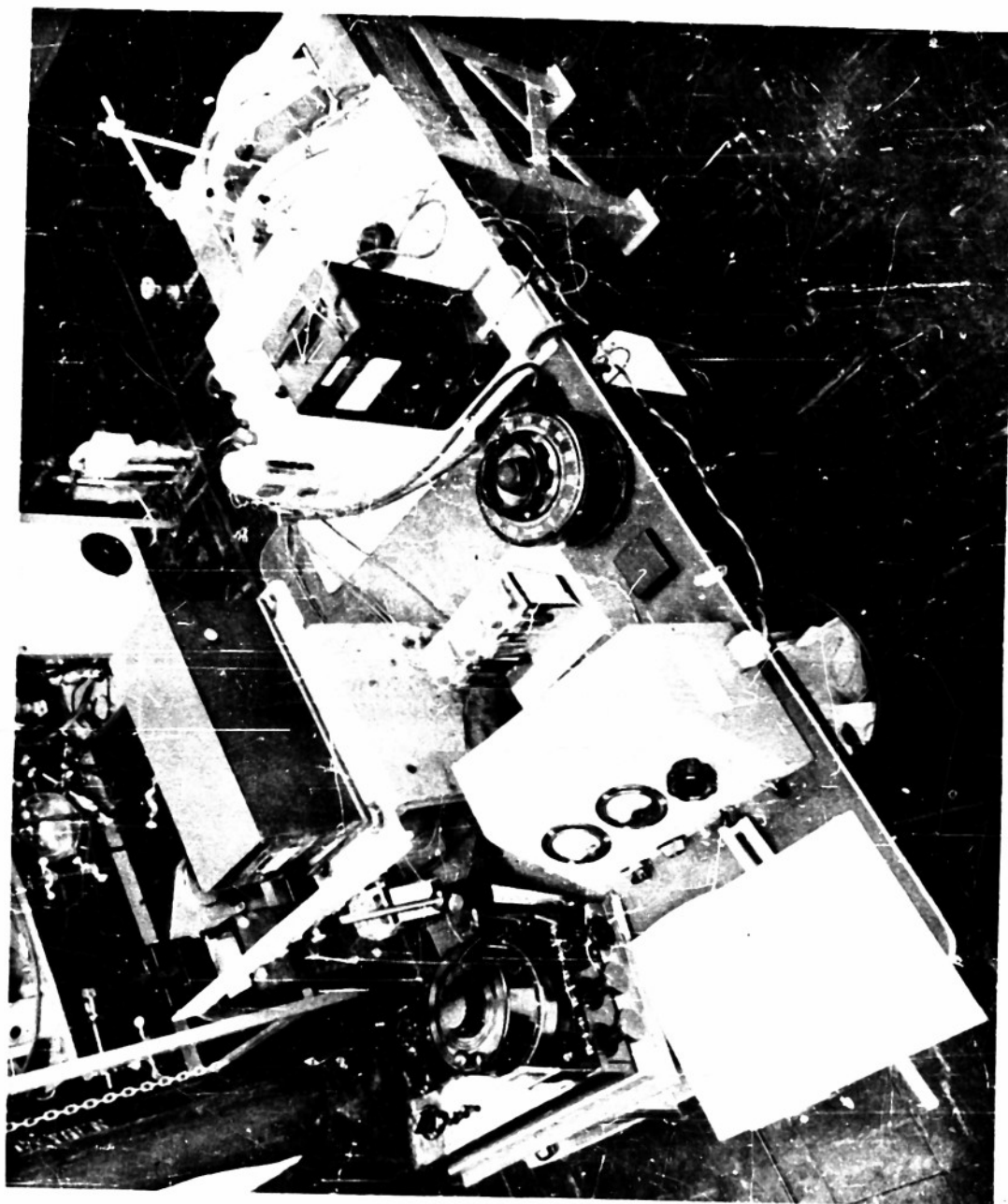


FIG. 4 APPARATUS USED FOR DETERMINING  
THE HALL EFFECT IN THIN FILMS

photoconductivity. The primary photo effect is the change in the number of conducting carriers resulting from the absorption of radiation. This is sometimes referred to as the "numbers" theory of photoconductivity. A secondary photo effect may exist in the presence of barriers which is a change in the barrier height resulting from the change in the number of carriers. This is referred to as the "barriers" theory of photoconductivity.

28. Scanlon, Petritz, and Lummis have found experimentally that lead sulfide responds according to a simple time exponential decay law. However, in the case of lead telluride, two decay processes were obtained--one following the exponential decay and the other the bimolecular or hyperbolic decay. On the basis of the numbers theory, they interpreted the existence of two time constants as representing a situation where one has a single conduction band with two lower energy states, one of which is normally filled.

#### Ultimate Sensitivity of Photoconducting Cells

29. Petritz has investigated the problem of noise in photoconductors through a theoretical treatment of the minimum detectable radiation signal for (a) the cell in thermal equilibrium with its surroundings and (b) the cell not in thermal equilibrium with its surroundings in which case the cell is exposed to radiation having a different temperature than the lattice temperature. In both cases he found the minimum detectable signal  $I_m(W.B.)$  to be

$$I_m(W.B.) = \frac{[(\bar{n}^2 - \bar{n}^2) A t]^{1/2}}{\gamma \tau} E_0 \quad (4)$$

where  $\bar{n}$  is the mean density of conduction electrons,  $E_0$  the energy difference between the two states involved in the process,  $\gamma$  the fraction of the power absorbed by the electronic system,  $\tau$  the time constant,  $A$  the film area, and  $t$  the film thickness. Equation (4) gives the minimum total amount of energy that can be detected during a period equal to  $\tau$ . The initials W.B. refer to a frequency band width sufficient to include the entire frequency spectrum of the cell. Among other factors, it is important to have a low statistical fluctuation in the number of conduction electrons in order to have a detector with high sensitivity as seen from equation (4). If the allowable frequency band is narrowed, Petritz finds

$$I_m(N.B.) = \frac{E_0}{\gamma} \left[ \frac{(\bar{n}^2 - \bar{n}^2) A t \Delta \omega_b}{\tau} \right]^{1/2} \quad (5)$$

30. It is of interest to relate the current noise as a function of the frequency. A spectrum of the noise can be determined



experimentally and provides a useful test of the theory. Such an expression has been developed by Petritz as

$$G(\Delta i^2) df = \frac{e b E^2 4 \tau df}{R [1 + (\omega \tau)^2]} + \frac{4 K \tau df}{R} \quad (6)$$

$$R = \frac{L}{A e b n} \text{ (resistivity)}$$

where  $L$  = length of film,  $b$  = mobility,  $E$  = electric field,  $\tau$  = time constant,  $n$  = carrier density, and  $G(\Delta i^2)$  is the amount of noise power lying in the frequency between  $f$  and  $f + df$ . The second term on the right hand side of the equation has been added to take into account the Johnson noise. Examination of this equation shows that one can obtain both the mobility and carrier density independent of Hall effect measurements. Equation (6) is also useful in determining, from the noise spectrum, when a cell is operating at, or close, to its ultimate sensitivity.

31. When numerical values are substituted in equation (6), we find that the minimum detectable signal for lead sulfide, as an example, is of the order of  $10^{-10}$  to  $10^{-11}$  watts/cm<sup>2</sup>.

32. Lummis and Petritz have shown that the second term appearing in equation (6) due to Johnson noise is very small in comparison to the first term or to the statistical fluctuation in the number of conduction electrons.

### Contact Noise

33. Current flow through a boundary between two different materials gives rise to contact differences of potential such as exist in rectifiers and transistors. The resistance of the contact is determined by the number of electrons in the neighborhood of the contact and their thermal energies. Petritz<sup>18</sup> has considered the theory of the noise of such a configuration which comprises the noise in bulk semiconductors, rectifiers, and transistors. Under conditions of steady current flow, Petritz has resolved the noise phenomena into the following related facts.

a. Existence of an excess noise which increases proportional to the square of the current where the existing noise is defined as the noise obtained after the Nyquist or Johnson noise power has been deducted. The Nyquist noise is expressed as  $4kTR\Delta f$ , which is the mean square voltage fluctuation in the frequency interval between  $f$  and  $f + \Delta f$ ,  $k$  is the Boltzmann's constant,  $T$  is the absolute temperature, and  $R$  is the resistance.

b. The noise spectrum is one that varies inversely proportional to the frequency and is known as the  $1/f$  law.

c. The existing noise is nearly temperature independent.

d. Noise of point contact devices is greater than that for corresponding p-n junction devices.

34. Petritz has resolved the above into two classes. Class one includes what can be called electronic noise and is due to fluctuations inherent in the electronic system of the material. Class two covers noise caused by the fluctuation of a quantity which modulates the average flow of current. Fluctuations under the first class can be described as fluctuations in the distribution of holes and electrons in various allowed energy states. Under class two, Petritz considers the phenomena to be one of "modulation noise", and he thinks of it in terms of a variable resistance. Petritz is able to show that the inherent noise in the electronic system of p-n junction devices, point contact devices, and bulk semiconductors can account for only a part of the observed noise and that noises of class two must be included before all of the noises can be accounted for. More specifically, modulation noise is required for those cases where the noise figures of transistors is greater than unity, where large differences exist between the noise figures of point contact and p-n junction transistors, and for the  $1/f$  portion of the noise spectrum.

#### Impurity Scattering

35. In studying the Hall effect in high purity germanium at low temperatures, a question arises as to the type of scattering that occurs between electrons and the lattice. Heretofore, it has been thought that ionic scattering predominates, but Petritz has offered an alternative explanation in which he proposed that electron scattering with neutral impurities offers a better explanation of the low temperature phenomena. He developed an approximate formula for the mean free path, based on the Born approximation method, which is in rough agreement with the experiments. Further refinements which include electron exchange were also considered.

#### Electroluminescence

36. It has been shown that an electric field applied to a phosphor excited by x-rays influences the light output of the phosphor. Such a phenomenon, called electroluminescence, has been examined in detail by Matossi and Nudelman using ultra-violet light in place of x-rays as a source of excitation. The mechanism giving rise to this phenomenon is not well understood and is the object of the present investigation. Quantitative information is being obtained concerning the effects of field strength, and wave shape of the applied field upon the nature of the radiating phosphor. Such information will provide data on the behavior of the transition of electrons from impurity levels to the conduction band under the presence of an external electric field.

## SECONDARY ELECTRON EMISSION

37. The mechanism of secondary electron emission can be considered in three parts: (a) the formation of electrons within the material by the primary electrons, (b) the diffusion of these electrons within the material; part of them reach the surface with certain amounts of kinetic energy, and (c) the escape of these electrons from the surface where they are identified as secondary electrons. Sternglass has examined these processes in considerable detail with respect to the atomic number of the material and to those electrons that are reflected from the surface and are identified as back-scattered electrons. The rate of diffusion of the electrons within the material to the surface depends upon the temperature of the material. As a result, the yield of the secondary electrons will be a function of the temperature. Sternglass has examined such temperature dependence for tantalum, platinum, and graphite; and he has found a decrease of the order of 0.6% per degree K as determined by measuring the variation in the peak height of the yield curve.

38. A recent theory of secondary electron emission proposed by Van der Ziel has been critically reviewed by Wayne R. Gruner<sup>5</sup>. An effort was made to improve Van der Ziel's treatment by correcting for the backscattering electrons and to make certain refinements in the theory. Gruner, however, was unable to improve the agreement between the experiments and theory by this treatment, which led him to believe that Van der Ziel's method was too approximate and that the theory should be amplified to coordinate the distribution of energy in the metallic electrons that are excited.

39. The problem of measuring the secondary electron emission from an insulating surface requires an arrangement whereby the potential of the emitting surface is under control. To accomplish this, one usually chops the beam of primary electrons in such a manner that the potential of the surface returns to its original value during the off-time, or by applying a potential intermittently to the target on which the material is deposited while the primary electron beam is held constant. In some instances these techniques are insufficient; and to meet such a situation, Scott developed a system whereby a combination of a doubled-pulsed primary and a pulsed back plate were used, synchronized in such a manner that the surface potential remained constant which enabled him to determine small variations in the secondary emission field.

## INFRARED RADIATION AND MOLECULAR STRUCTURE

40. It is usually considered that only a change in the dipole moment will give rise to absorption, which explains why gases

such as oxygen show no appreciable absorption in the infrared under usual conditions. This has led to the conception that usually the absorption by induced dipoles should be weak. Matossi has noted that there are exceptions to this situation, particularly in homopolar gases such as  $\text{ICl}$  or  $\text{FCl}$ . He has considered this problem from a classical standpoint and has described the observed dipole moments as an interaction of charges that give rise to two terms in the expression for the absorption if it could be shown that the absorption in these molecules is due to induced dipoles and to their change during the molecular vibration. Such a postulate does not require the actual existence of ions or even ionic binding. He showed that this model gives correct orders of magnitude for the absorption.

#### Classical Model of Molecular Dipoles and Polarizabilities

41. Matossi has formulated a classical model of molecular dipoles and polarizabilities that is determined by the behavior of induced atomic dipoles. He modified older theories, in particular the Silberstein model of optical anisotropy which describes the optical properties of molecules in terms of interacting induced dipoles. Serious difficulties arise with the Silberstein model since it does not describe the observations as being quantitatively correct. Matossi, following a remark by Mott and Gurney, has introduced a modification involving an overlapping of the fields of the interacting induced dipoles. Through a sort of screen factor and by considering the variability of the atomic polarizabilities in electric fields, Matossi was able to apply the Silberstein model to molecular refraction, Rayleigh scattering, Kerr effect, Raman effect, and the calculation of infrared intensities for  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{Cl}_2$ ,  $\text{CO}_2$ , and  $\text{CS}_2$ . Such a treatment was found applicable to a semiquantitative treatment of infrared absorption in di-substituted benzenes.

#### The Structure of Oxide Glasses

42. Anderson and Matossi have formulated a relationship between the infrared reflection spectrum and the structure of glasses. They have shown that certain glass constituents, normally considered as glass modifiers, could be spectroscopically detected as well as other constituents existing in the material. They were concerned with the vibration damping of coordinated units, and were able to show that the glass does not respond as a completely random network as usually considered in such an amorphous material.

#### A Source of Infrared Radiation

43. Molecules in a gas phase when properly excited are known to emit radiation characteristic of their energy states. There

apparently has been little work done on such emission spectra of gaseous molecules in the infrared. This subject was reopened by Talley, Lowe, and Scanlon in the case of  $\text{CO}_2$  and other gases. The excited gas was contained in a conventional type of discharge tube. A differentiation between the radiation from the gas and from the walls was accomplished by exciting the gas with an alternating potential. Emission from the gas was observed at  $3600 \text{ cm}^{-1}$  and  $2300 \text{ cm}^{-1}$ , which is identified as being due to  $\text{CO}_2$ . Other gases such as methane, ethane, and others were also found to emit radiation in the region of  $3000 \text{ cm}^{-1}$ .

## GEOMETRICAL OPTICS

44. The problem of the third order lens aberration has frequently arisen in connection with investigation of lens design being conducted by Mahan. As a result of frequent requests to discuss this subject, a formal presentation of the problem was made. It is of interest to examine the unusual shapes and colors of the aberration patterns which are formed. Figure 5 illustrates an example of zonal patterns for a plano-convex lens. Through such a study of imaging problems, with large zonal patterns, the more difficult investigation of the situation when the patterns become small can be more easily solved.

## SERVICES

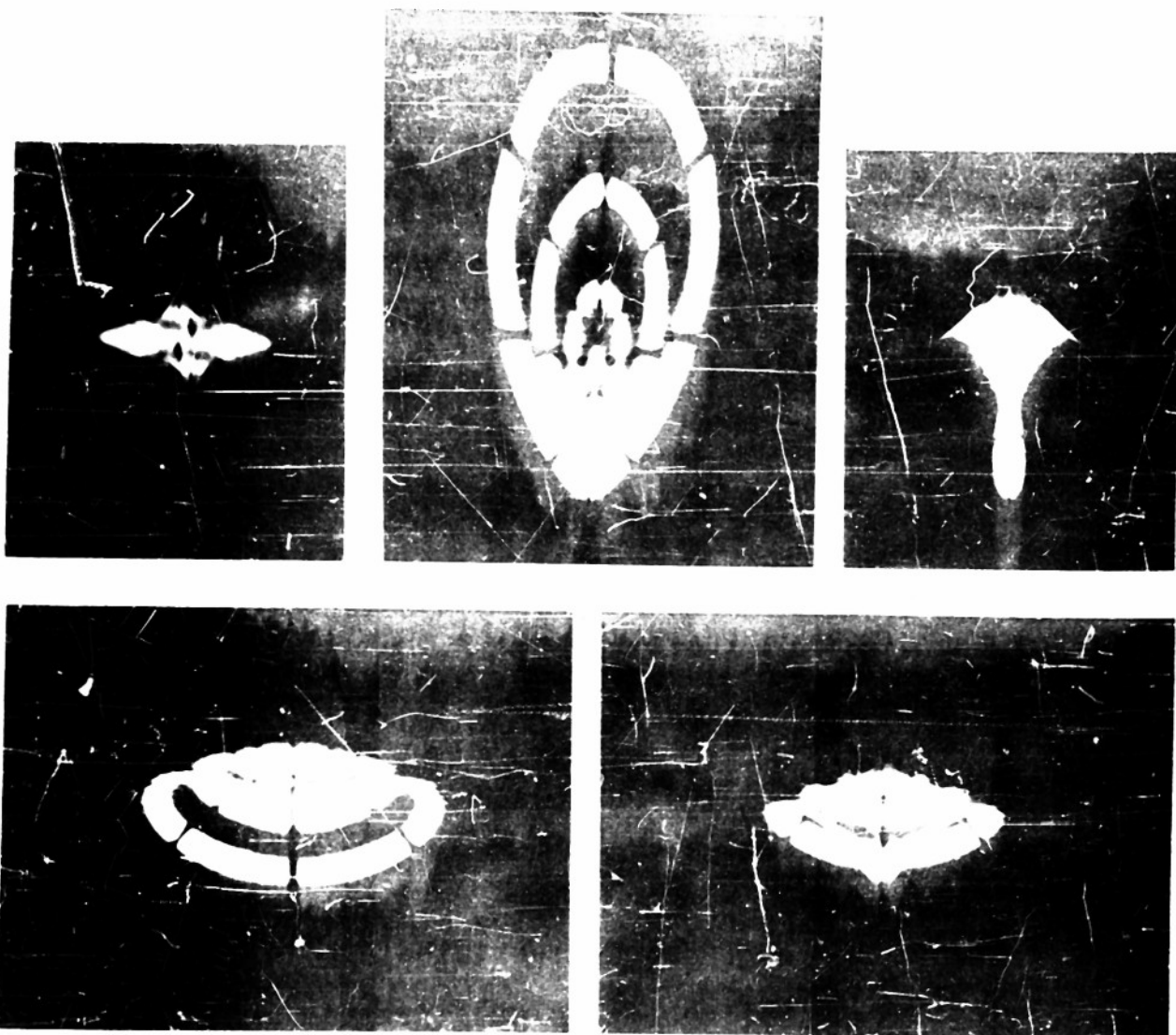
45. Certain facilities in the Solid State Division are used for services to the various departments in this Laboratory.

### Spectroscopic Analysis

46. Through the use of infrared and visible spectrographs, Marion Glickman carried out the following analyses:

- a. Decomposition products of primer explosions
- b. Traces of impurities on relay contacts
- c. Nitroguanidine and its decomposition products
- d. Ethyl nitrate and associated decomposition products
- e. Search for niobium and titanium in sample furnished by UM
- f. Analysis of explosive primer
- g. Analysis of iron in  $\text{CaSO}_4$

# RAYONNEMENTS



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- h. Magnesium aluminum phosphide flares
- i. Analysis of components of captured ordnance equipment
- j. Analysis of 10 gauges for Engineering Department
- k. Major components of unknown sample
- l. Analysis of strontium titanates
- m. Search for impurities in 35 liquid and solid solutions submitted by Engineering Department
- n. Infrared absorption of samples containing  $\text{CCl}_4$  with aluminum stearate in suspension
- o. Analysis of plug contacts
- p. Others not itemized

See Figure 6 for photograph of infrared equipment used for analysis.

47. Through the use of our mass spectrometer, Spriggs, in addition to his work on certain other projects, performed gas analysis of samples covering 15 separate specimens submitted by the Explosives Research Department, and a study was made for this department of molecules having low molecular weight.

## REPORTS AND PUBLICATIONS

### Naval Ordnance Reports

- 1 Navord 1844, "AC Magnetic Properties of Ferrocube III", W. W. Talbert, 14 Jan 1952, Unclassified
- 2 Navord 2292, "Feasibility Report on Infrared Image Formation by Secondary Electron Emission from Dielectrics in the 8-13 $\mu$  Wavelength Region", E. J. Sternglass, E. J. Scott, and L. R. Maxwell, 4 Jan 1952, Confidential
- 3 Navord 2423, "The Feasibility of Detecting the Water Entry of Aircraft-Laid Mines by Infrared Techniques", D. S. Lowe and R. M. Talley, 3 Jul 1952, Secret
- 4 Navord 2457, "Capacitance Effects in Thin Conductive Films", J. N. Humphrey, F. L. Lummis, and W. W. Scanlon, 8 Jul 1952, Unclassified
- 5 Navord 2469, "Note on Van der Ziel's Model of Secondary Electron Emission at Low Primary Energies", Wayne R. Gruner, 8 Jul 1952, Unclassified



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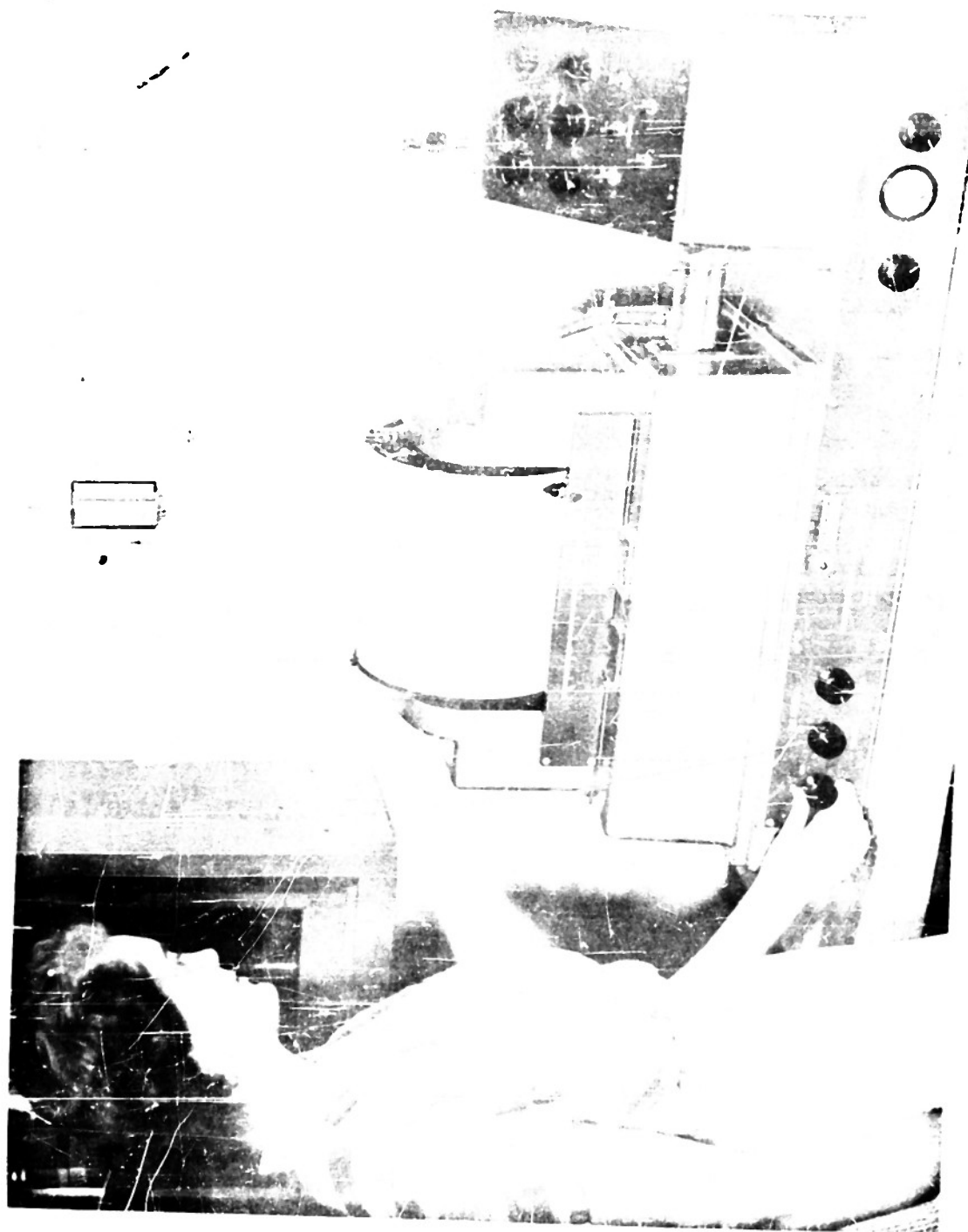


FIG. 6 RECORDING INFRARED SPECTROMETER  
USED FOR ANALYSIS OF MATERIALS

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- 6 Navord 2310, "Attainments of the Solid State & Optics Research Division During Calendar Year 1951", D. F. Bleil, 4 Feb 1952, Confidential

In addition to the above Naval Ordnance Reports, informal memoranda were written by Greenwald, Perros, Lowe, Talley, Wangness, Smart, McGuire, and Matossi.

Papers Published in Journals Outside the Laboratory

- 7 "The Magnetic Susceptibility of Uranium" by C. J. Kriessman and T. R. McGuire, Phys. Rev. 85, 452 (1952)
- 8 "The Magnetic Susceptibility of Chromium" by T. R. McGuire and C. J. Kriessman, Phys. Rev. 85, 452 (1952)
- 9 "Polarizability Model of Effective Charges" by Frank Matossi, J. Chem. Phys. 20, 819 (1952)
- 10 "An Exact Early Solution for the Reflectance of Reflection-increasing and Reflection-reducing Films" by Archie I. Mahan, J. Opt. Soc. Am. 42, 259, (1952)
- 11 "Magnetic Resonance in a System Containing Two Magnetic Sublattices" by Roald K. Wangness, Phys. Rev. 86, 146 (1952)
- 12 "On the Molecular Field Treatment of Ferromagnetism and Antiferromagnetism" by J. Samuel Smart, Phys. Rev. 86, 968 (1952)
- 13 "A Theory of Contact Noise" by Richard L. Petritz (letter to the editor) Phys. Rev. 87, 535 (1952)
- 14 "Microwave Resonance Absorption in Antiferromagnetic Materials" by Louis R. Maxwell, Am. J. Phys. 20, 80 (1952)
- 15 "Exchange Coupling and the Curie-Weiss Law" by R. K. Wangness, J. Chem. Phys. 20, 1656 (1952)
- 16 "A Modified Silberstein Model of Optical Anisotropy" by Frank Matossi, J. Chem. Phys. 20, 1934 (1952)
- 17 "On the Anomaly in the Heat Capacity of Manganous Oxide" by R. K. Wangness, Science 116, 537 (1952)
- 18 "Theory of Noise in P-N Junctions and Related Devices" by R. L. Petritz, Proc. I.R.E. 40, 1440 (1952)
- 19 "Infrared Molecular Emission Excited in a Glow Discharge" by R. M. Talley, D. S. Lowe, and W. W. Scanlon, J. Opt. Soc. Am. 42, 982 (1952)

- 20 "Magnetic Properties of the Chromites" by T. R. McGuire, Louis N. Howard, and J. Samuel Smart, Ceramic Age, 60, 22 (1952)

PAPERS PRESENTED AT MEETINGS OUTSIDE THE LABORATORY

- 21 "The Magnetic Properties of the Chromites" by T. R. McGuire, Louis N. Howard, and J. Samuel Smart, American Physical Society Meeting, New York, N. Y., 31 Jan-2 Feb 1952
- 22 "Magnetic Resonance in a System Containing Two Magnetic Sublattices" by Roald K. Wangsness, American Physical Society Meeting, Columbus, Ohio, 20-22 March 1952
- 23 "The Impedance of the Semiconducting Films" by J. N. Humphrey, F. L. Lummis, and W. W. Scanlon, American Physical Society Meeting, Columbus, Ohio, 20-22 March 1952
- 24 "The Relation between Noise and Response Time in Photoconductors: I Theory" by R. L. Petritz, American Physical Society Meeting, Columbus, Ohio, 20-22 March 1952
- 25 "The Relation between Noise and Response Time in Photoconductors: II Experiment" by F. L. Lummis and R. L. Petritz, American Physical Society Meeting, Columbus, Ohio, 20-22 March 1952
- 26 "Multiple Time Constants in Photoconductivity" by W. W. Scanlon, R. L. Petritz, and F. L. Lummis, American Physical Society Meeting, Columbus, Ohio, 20-22 March 1952
- 27 "Some Geometrical, Physical, and Physiological Aspects of Light" by A. I. Mahan, Philosophical Society of Washington, 25 April 1952
- 28 "Modification of the Silberstein Model of Optical Anisotropy" by Frank Matossi, American Physical Society, Washington, D. C., 1-3 May 1952
- 29 "The Magnetic Susceptibility of Cb, Ta, V, Mo, and W at High Temperatures" by C. J. Kriessman, American Physical Society, Washington, D. C., 1-3 May 1952
- 30 "On the Diffusion Theory of Noise in Rectifiers and Transistors" by R. L. Petritz, American Physical Society, Washington, D. C., 1-3 May 1952
- 31 "Intensity of Infrared Absorption by Induced Dipoles" by Frank Matossi, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 8-13 June 1952
- 32 "Third Order Methods in Lens Design" by A. I. Mahan, presented at Johns Hopkins University, Baltimore, Maryland, 11 May 1952

- 33 "Some Considerations of the Relationship between the Infra-red Spectrum and Structure of Oxide Glasses" by Frank Matcossi, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, 8-13 June 1952
- 34 "Microwave Resonance Absorption in Antiferromagnetic Materials" by L. R. Maxwell, T. R. McGuire, Symposium on Magnetism, College Park, Maryland, 2-6 Sep 1952
- 35 "The Magnetic Susceptibility of TiO and Vo" by T. R. McGuire, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 36 "Magnetic Susceptibility of V, Cr, Ta, Mo, and W at High Temperatures" by C. J. Kriessman, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 37 "The Molecular Field Treatment of Antiferromagnetism" by J. Samuel Smart, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 38 "Antiferromagnetic Resonance" by L. R. Maxwell and T. R. McGuire, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 39 "Temperature Dependence of the Magnetic Susceptibility of the Transition Elements" by C. J. Kriessman, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 40 "The Molecular Field Treatment of Antiferromagnetism" by J. Samuel Smart, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 41 "The High Temperature Magnetic Susceptibility of V, Nb, Ta, W, and Mo" by C. J. Kriessman, Symposium on Magnetism, College Park, Md., 2-6 Sep 1952
- 42 "On the theory of Impurity Scattering in Semiconductors" by R. L. Petritz, Solid State Conference, Purdue University, Lafayette, Indiana, 27-29 Sep 1952
- 43 "Magnetic Structure Transitions" by J. Samuel Smart, Thermodynamics Colloquium, Bureau of Standards, Washington, D.C., 2 Oct 1952
- 44 "Zonal Aberration Patterns of Long Focal Length Single Lenses" by A. I. Mahan and H. A. Templin, Optical Society of America, Boston, Mass., 9-11 Oct 1952
- 45 "Infrared Molecular Emission Excited in A Glow Discharge" by D. S. Lowe, R. M. Talley, and W. W. Scanlon, Optical Society of America, Boston, Mass., 9-11 Oct 1952

- 46 "A Technique for Secondary Electron Emission Measurements"  
by E. J. Scott, American Physical Society, St. Louis, Mo.,  
28-29 Nov 1952

#### AWARDS, PATENTS, AND OFFICES HELD

##### Awards

Meritorious Civilian Service Award - Louis R. Maxwell, Dec 1952

##### Patents

Application for Electromagnet patent by Louis R. Maxwell, Navy  
Case No. 13,984

##### Offices Held

Dr. Archie I. Mahan was elected to the office of president of  
the Philosophical Society of Washington

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