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THERMAL MEASUREMENTS ON SOLIDS

BELOW 1 K

by

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Thermal Measurements on Solids Below 1 K

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This report summarizes the work done on this project from February, 1971 to the present. The participating staff consisted of H. Weinstock (Associate Professor of Physics), C. Chau (Assistant Professor of Physics), D.S. Kupperman, W. Thys and G. Kurz (Research Associates), the following graduate students: B. Vis, S. Lu, and J. Ho; and undergraduate students: M. Mueller and J. Parpia.

I. Summary of Research Progress

A. Thermal Conductivity of Neutron Irradiated MgO

In the previous Progress Report (No. 5), the results of thermal conductivity measurements between 0.4 and 100 K were presented for two relatively pure specimens of common origin: one unirradiated, the other with a total dose of 2×10^{18} neutrons/cm². Resonant type reductions or dips in the conductivity were observed at about 1 K and 20 K. This work has now been extended to include measurements over the same temperature range for two additional specimen crystals (cut from the same boule) with radiation doses of 4×10^{17} and 2×10^{19} neutrons/cm².

The results of the earlier and more recent thermal conductivity measurements are presented in Fig. 1. It is observed that while the

resonant dip at 20 K becomes more pronounced with increasing neutron dose, the dip at about 1.1 K disappears completely for the 2×10^{19} neutrons/cm² and is most evident for the 4×10^{17} neutrons/cm² dosage. Radiation sensitive changes in thermal behavior are seen more clearly in Fig. 2 where a plot of reduced thermal resistivity versus temperature has been made. In the case of both resistive peaks, there is no shift in peak temperature with neutron dose.

Recent optical studies of n-irradiated MgO have indicated the concentration of F^+ centers increases with increasing neutron dose.¹ Since the resonant thermal resistivity also increases with increasing neutron irradiation at 20 K, and the temperature of the resonance does not shift, it is tentatively proposed that the 20 K resonance is associated with a quasi-localized mode of the F^+ center. More recently, Y. Chen of Oak Ridge National Laboratory has presented evidence for the existence of defect aggregates in MgO which are most likely anion divacancies.² Although the resonance centered at 1.1 K is not yet understood, it may be associated with vibronic levels of small aggregates or interstitial clusters.

The current studies in MgO are being continued and extended. At the present time, a computer analysis of the thermal conductivity data, based on the Debye model of solids, is being carried out to determine the resonance frequencies and to explain the nature of the resonances and large decrease in thermal conductivity due to neutron irradiation. In order to distinguish between geometrical scattering and vibronic modes, measurements of the difference in specific heat between the irradiated and pure crystals are being planned.

B. Thermal Conductivity of Lead Films in the Intermediate Superconducting State.

When a type I superconductor is cooled below its transition temperature (T_c) and subsequently exposed to a magnetic field perpendicular to its largest surface, an intermediate state results which is characterized by a partial penetration of magnetic flux into the superconductor. Huebener et al³ found, in their magneto-optical observations for superconductor lead films with thickness greater than $1\mu\text{m}$, a structure of the intermediate state which agrees reasonably with the laminar model developed by Landau⁴. The Landau model predicts long normal domains randomly distributed over a superconducting matrix. As the external field is increased, the width of the domains grows until the critical field is reached. Beyond this field value, the entire sample is in the normal state.

The main purpose of the current investigation is to study the scattering of electrons and phonons at the normal-superconducting phase boundaries. The scattering potential associated with these boundaries is the electron pair potential Δ , which is equal to the energy gap inside the superconducting regions and drops to zero in the normal regions. Since only the normal electrons and the phonons are scattered at the phase boundaries, and since these are the heat carriers, thermal conductivity is a suitable means to study this scattering.

The specimen is a lead film $4\mu\text{m}$ thick, with a critical temperature of 7.2 K. Figure 3 shows the thermal conductivity of the lead film as a function of temperature. This behavior agrees surprisingly well with the result found by other authors⁵ for bulk lead and is characteristic of superconductors with a small Debye temperature and a fairly high superconducting transition temperature.

As expected⁶, a minimum at about $H_c/2$ was observed in the thermal conductivity - see Fig. 4 - as a function of the external magnetic field both in the low temperature range where phonons make the major contribution to the thermal conductivity in the superconducting state and at higher temperatures where electron transport dominates. Both the depth of the minimum and the reduced field value at which it occurs are temperature dependent. The minimum occurs because the scattering of the normal electrons and phonons at the phase boundaries decreases the thermal conductivity more than the penetration of magnetic flux into the sample increases it.

The small dip in the conductivity just above the critical field has never been observed before, and it is not yet understood completely. There is strong indication that this behavior is related to order parameter fluctuations. Further experimental work is required to understand this anomaly.

Thus far no systematic experimental study of the scattering process underlying the minimum in the conductivity has been made because the scattering angle is random over the sample. However, Huebener⁷ has shown that an electric current pulse applied perpendicular to the magnetic field and exceeding the depinning threshold current rearranges the magnetic flux into a more ordered structure. This structure will be frozen-in provided the flux pinning in the film is high enough to overcome internal forces in the flux structure. Adequate flux pinning has been achieved by evaporating the lead film onto a cooled substrate.

A 1.5 A high and 1 msec broad current pulse was applied in the direction of the heat flow to be used in the thermal conductivity measurements. As a result, the flux domains align perpendicular to the applied heat flow (as observed by Huebener et al³). In Fig. 4 a plot has also been made of the

thermal conductivity as a function of the external magnetic field, for a fixed $T = 3.77$ K, after the current pulse has been applied. The measuring procedure is as follows: the magnetic field is increased to a chosen value, and the conductivity is measured before and after the current pulse is applied. In order to wash out possible remaining effects of the current pulse, the field is then reduced to zero before changing it to the next higher value. It is noted that the conductivity is lower after the current pulse has been applied, at least at the lower fields. This is in agreement with the fact that aligning the laminae in a direction perpendicular to the heat flow increases the scattering cross section at the phase boundaries. At higher fields, however, the conductivity is higher after the current pulse, indicating that the geometry of the flux domains might have changed in an appropriate fashion. This is not obvious from the magneto-optical work of Huebener et al³. More experimental work is required, especially as a function of temperature and pulse width. Flux flow measurements combined with thermal conductivity measurements are planned.

C. Radiation Damage of Amorphous Carbon Films

In recent years, attempts have been made to use thin films for heavy-ion strippers in electrostatic accelerators to obtain particles in higher charge states with correspondingly higher energies after acceleration. However, the practical use of such films has been limited by the rapid destruction of the films under heavy ion bombardment of less than one hour's duration. A research project is currently in progress at Argonne National Laboratory (ANL) under the direction of Dr. J. L. Yntema to provide a reliable source of highly charged ($\sim + 50e$) heavy ions by use of a carbon film stripping reaction. The current study at IIT was ini-

tiated as a collaborative effort with the ANL group to study the properties of these carbon thin films, especially radiation damaged films, with the hope of shedding some light on the technology of prolonging the film lifetime. As in often the case, this study is proving to be of basic (vis-a-vis amorphous semiconductor) as well as practical interest.

In undertaking this investigation, several experimental techniques have been employed, e.g., electrical resistivity, X-ray back scattering and optical absorption. The carbon films used in this experiment are from two commercial sources. Each supplier has used a similar evaporation technique, but growth rates of the films are most likely different. The nominal thickness of the samples is $500 \text{ \AA}$. The room temperature electrical resistivity varies by as much as two orders of magnitude for samples from the two different sources.

The resistivity of these carbon films has been measured, at first, as a function of temperature from 300 to 1100 K. A typical resistivity versus temperature curve is shown in Fig. 5. Up to the temperature of 450 K, the sample is heated under vacuum, and above 450 K the sample is surrounded by nitrogen gas. Under this process of heat treatment, the resistivity (of the lowest resistivity specimens) decreases toward higher temperatures by more than a factor of 20 between the extremes of 300 and 1100 K. This behavior is interpreted as follows. Gas molecules were trapped within the carbon film during its deposition on the glass substrate. The amount of trapped gas molecules depends on the growth rate and the quality of vacuum inside the evaporator. These gas molecules may be responsible for the large deviation of room temperature resistivity of films from the two suppliers. When a film is heated in vacuum, gas molecules are liberated from the carbon film, leaving it with donor type regions which are a source of conduction electrons.

Therefore, the resistivity decreases as gas molecules are removed. A similar phenomenon is observed in bulk carbon⁸. This explanation appears plausible as heat treatment on two samples with room temperature resistivities differing by a factor of over 100 before treatment, reduces the resistivities to the same magnitude after treatment.

In Fig. 5, the $\ln \rho$ versus $1/T$ is also presented. The slope of this curve provides a direct measure of the energy band gap of the carbon film. The band gap varies from 0.26 eV to 0.12 eV for temperatures above 680 K. Due to the reflectivity of the sample, it is possible only to estimate the absorption band edge to be less than 0.3 eV using infrared optical measurements. This result is in good agreement with the observation by Levy-Mannheim and Mering⁹ on similar samples. Mrozowski⁸ has pointed out that the energy band gap of carbon decreases with increasing crystallite size. The present results definitely indicate a decreasing energy band gap for annealing temperatures above 680 K. This implies that the crystallite size is enlarged by the annealing process.

More recently, the resistivity measurements on the films have been extended downward to 3 K. When carbon atoms are deposited on a cold substrate, the carbon film may be in an amorphous state. Thus, these films could be useful in the study of electronic conduction in non-crystalline solids. The resistivity of one sample below 4 K is shown in Fig. 6. The resulting curve indicates that $\ln \rho$ deviates from the $T^{-1/4}$ dependence predicted by Mott¹⁰. However, an X-ray photograph reveals a very faint ring which suggests that the sample may not be completely amorphous. To pursue this study, it will be necessary to deposit on a liquid nitrogen cooled substrate, in order to ensure a completely amorphous state of the carbon film.

Currently, resistivity and annealing studies are being carried out

on specimens having been irradiated in a Ni ion beam of the Dynamitron at NAL.

D. Transport Measurements in Pyrolytic Graphite

The basal plane thermal and electrical conductivity of highly oriented pyrolytic graphite samples have been measured from 0.34 to 4.0 K in an external magnetic field up to 23 kG. In this work it is possible to separate the lattice thermal conductivity from the electronic thermal conductivity. These results have been given in Progress Report No. 5. At that time, the interpretation made considered the lattice conductivity to be limited by the boundary scattering and yielded the following expression for thermal conductivity:

$$K_a = \ell_a \sum_p C_p \langle v_p \rangle_a \quad (1)$$

where p is the normal mode index, ℓ_a is the mean free path along the basal plane, C_p is the specific heat of p mode and $\langle v_p \rangle$ is the average group velocity along the basal plane. In this expression it is assumed that the mean free path perpendicular to the basal plane ℓ_c is much larger than ℓ_a . Using Komatsu's¹¹ calculated specific heat and an appropriate average group velocity at 2 K, it is found that ℓ_a is about 20 microns. However, Eq. 1 applies only for boundary scattering and can not be extended to include other frequency dependent phonon scattering processes such as fast neutron produced defect scattering. One must start with a general lattice conductivity expression in terms of a combined relaxation rate for all phonons. An appropriate expression for the basal plane conductivity is

$$K_a = k_B \left(\frac{h}{k_B T} \right)^2 \sum_{p, \sigma} v_p^2(\vec{\sigma}) \tau_p(\vec{\sigma}) \frac{e^{h\nu_p/k_B T}}{e^{h\nu_p/k_B T} - 1} \left\{ v_p(\vec{\sigma}) \right\}_x^2 \quad (2)$$

where $\vec{\sigma}$ is the phonon wave vector, $v_p(\vec{\sigma})$ is the phonon frequency and $\{v_p(\vec{\sigma})\}$ is the phonon group velocity. According to the crystallographic structure of graphite, the first Brillouin zone can be represented by a cyclindrical surface. Using the Debye approximation, the summation over wave vectors is replaced by an integral. Then the lattice thermal conductivity is the sum of three integrals which correspond to the two in-plane longitudinal and transverse modes and one out-of-plane mode. The combined relaxation rate $1/\tau_p(\vec{\sigma})$ in Eq. 2 characterizes all possible scattering processes. Under the usual relaxation time approximation, $1/\tau_p(\vec{\sigma})$ is

$$1/\tau_p(\vec{\sigma}) = 1/\tau_p(\vec{\sigma})_{\text{boundary}} + 1/\tau_p(\vec{\sigma})_{\text{defect}} \quad (3)$$

The boundary relaxation rate is expressed as

$$1/\tau_p(\vec{\sigma})_{\text{boundary}} = \{v_p(\vec{\sigma})\}_a / \ell_a + \{v_p(\vec{\sigma})\}_c / \ell_c \quad (4)$$

Due to the anharmonicity of graphite, one must include boundary scattering for all phonons even though some may not be travelling along the direction of the temperature gradient. The second term on the right hand side in Eq. 4 is frequently neglected by many authors^{12,13} with the assumption that $\ell_c \gg \ell_a$. However, this assumption is incorrect for the data obtained in the current study. It is found that the lattice conductivity below 1 K exhibits a T^3 dependence. Careful study of the three thermal conductivity integrals will indicate that for $\ell_c \gg \ell_a$ the conductivity will have a T^2 dependence contrary to the experimental results. In fact, it is found that ℓ_a must be larger than ℓ_c to obtain a fit to the data in this work. Using this theoretical model, an analysis of the thermal conductivity of radiation damaged graphite may be made.

E. Thermal Conductivity of Superconducting Alloys

Measurements on commercially available Va_3Ga ribbon and NiTi wire supplied by Dr. Carl Henning of the Lawrence Radiation Laboratory have been carried out between 1 and 25 K, and as a function of applied magnetic field. Results of these measurements have been supplied to Dr. Henning and to Dr. W. C. Overton, Jr. of the Los Alamos Scientific Laboratory for use in their studies related to high field magnets for controlled nuclear fusion devices. The thermal conductivity measurements performed are a prelude to a more extensive series of measurements to be carried out on superconducting wires and ribbons with insulating coatings included. The major aim of this work is to provide thermal information related to determining the speed of heat removal when sections of a superconducting magnet revert to the normal metallic state.

Another study on the thermal conductivity of a series of La-Gd-In alloys will commence shortly when the specimens, now being prepared by Dr. Joseph Darby of ANL, are made available.

F. Specific Heat of $UO_2Rb(NO_3)_3$

Measurements have now been completed over the temperature range 0.5 to 20 K on a ^{235}U rich specimen salt. Earlier work on a sample of normal (mostly ^{238}U) isotopic uranium showed that the salt was not in good thermal contact with its copper containing vessel, and it was returned to Oak Ridge National Laboratory for repacking.

The weak heat link method of heat capacity measurement¹⁴ was used successfully in overcoming the problem created by the sizable self heating due to α particle emission in the ^{235}U rich salt. Unfortunately, no strong evidence was found for a nuclear Schottky anomaly tail (related to nuclear electric quadrupole coupling) even at the low end of the measured temperature range.

Some evidence of this $1/T^2$ dependence may be present, but analysis is complicated by the observation of a Schottky like peak in heat capacity in the vicinity of 2 K. This peak cannot be related to the ^{235}U nuclei as its magnitude is two orders of magnitude too small for this. Most likely, it is related to an impurity of about 1% concentration.

It appears likely that the self heating of the ^{235}U rich salt may prevent a measurement of heat capacity below 0.5 K, even using a helium dilution refrigerator, although an attempt may be made (when time permits) to conduct such an experiment.

G. Thermal Measurements on Antiferromagnetic Insulators

Earlier work on the thermal conductivity of cobalt chloride thiourea has been submitted for publication. Currently a new set of these crystals is being grown from solution for use as specimens for both thermal conductivity and heat capacity measurements as a function of both magnetic field and temperature utilizing a helium dilution refrigerator and 60 kG superconducting magnet. Other species of antiferromagnetic insulating crystals are in the process of being grown.

A series of heat capacity measurements on powdered specimens of tetramethylammonium manganese chloride and tetramethylammonium cadmium chloride will commence shortly. The purpose of this study is to determine the exchange constants related to magnetic linear chains.

II. Summary of Publications: January, 1971 to the present

"Magnon Conductivity in Antiferromagnetic Cobalt Chloride Thiourea," C. Ni and H. Weinstock, Phys. Letters 34A, 3 (1971) (C00-1629-14)

"Effect of Colloids on the Thermal Conductivity of γ -Irradiated KCl," R. A. Guenther and H. Weinstock, J. Appl. Phys. 42, 3790 (1971) (C00-1629-21)

G. Kurz and S. Sussman, Phys. Stat. Solidi (b) 46, 1(K5-K7) July 1971 (C00-1629-25)

"Spin Wave Conductivity in Antiferromagnetic Cobalt Chloride Thiourea, $\text{CoCl}_2[(\text{NH}_2)_2\text{CS}]_4$," C. Ni and H. Weinstock, Bull. Am. Phys. Soc. 16, 403 (1971) (C00-1629-19)

"Thermal Conductivity of Neutron Irradiated MgO ," G. Kurz and H. Weinstock, Bull. Am. Phys. Soc. 16, 383 (1971) (C00-1629-23)

"Magneto-Thermal Conductivity of Pyrolytic Graphite," S. Y. Lu and C. K. Chau, Bull. Am. Phys. Soc. 16, 384 (1971) (C00-1629-18)

"Survey of Thermometric Characteristics of Recently Produced Allen-Bradley/Ohmite Resistors," H. Weinstock and J. Parpia, Temperature 4 (to be published) (C00-1629-22)

"Phonon Resonant Scattering in CdS Containing Co^{2+} ," C. K. Chau, Phys. Rev. (accepted for publication) (C00-1629-26)

"Magneto-Thermal Properties of Heat Transport in Cobalt Chloride Thiourea," C. Ni, H. N. Spector and H. Weinstock, Phys. Rev. (submitted for publication) (C00-1629-27)

"Electrical Resistivity of Carbon Films," C. K. Chau and D. S. Kupperman, Bull. Am. Phys. Soc. (March 1972) (C00-1629-28)

"Thermal Resonances in Neutron Irradiated MgO ," D. S. Kupperman, G. Kurz and H. Weinstock, Bull. Am. Phys. Soc. (March 1972) (C00-1629-29)

"Thermal Conductivity of Thin Film Lead," W. Thys, C. K. Chau and H. Weinstock, Bull. Am. Phys. Soc. (March 1972) (C00-1629-30)

III. Graduate Student Progress

Three students are currently employed in research activities under this project.

Benjamin Vis has completed all requirements, except that relating to a thesis, for a Ph.D. degree. He has carried out heat capacity measurements on uranium salts preliminary to his current thesis research (just commencing) on the heat capacity of various antiferromagnetic insulators.

Shui-Ying Lu has also completed all graduate school requirements, except that for the Ph.D. thesis. Earlier she had carried out research for an M.S. thesis on the thermal and electrical conductivity of pyrolytic graphite. Her Ph.D. thesis research, begun in January, 1972, is centered on low temperature thermal and electrical conductivity measurements of the Kondo alloys, Cu:Fe and Cu:Cr (where the Fe and Cr impurity content is on the order of hundreds of parts per million).

Jen-Lie Ho is a second year graduate student with a perfect 4.0/4.0 academic average. He qualified for Ph.D. candidacy on his first attempt to do so. His first association with this project came during the summer of 1971. Currently he is engaged in learning the various experimental techniques of the laboratory and, in particular, setting up the circuitry for the magnetic thermometry in the helium dilution refrigerator. It is expected that he will commence work on a Ph.D. thesis problem by the summer or fall of 1972.

IV. Progress in the Development of Laboratory Facilities

Due to an abundance of both well qualified investigators and interesting research problems, a third experimental station for measurements above 4 K

has been established. This has been done mainly utilizing "spare parts" such as a 4" I.D. glass liquid helium-liquid nitrogen dewar set and various vacuum system components. Also, to relieve the demand on the three existing experimental cryostats for use in the laboratory's original cryogenic station, a fourth such cryostat is under construction. This will be an improved version over the existing models in that it will contain a 1 K ^4He bath in addition to a 0.3 K ^3He bath, allowing for continuous field variation of a superconducting magnet which will surround the cryostat in a ^4He bath at 4.2 K. In the present cryostats, the superconducting magnet is usually situated in a ^4He bath at about 1 K, and only persistent mode operation of the magnet ensures that temperature stability can be maintained by the ^3He bath.

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Fig. 1 Thermal conductivity vs. temperature for "pure" and neutron irradiated MgO.

Fig. 2 Reduced thermal resistivity vs. temperature for neutron irradiated MgO.

Fig. 3 Thermal conductivity vs. temperature for 4μ thick lead film

Fig. 4 Thermal conductivity vs. applied magnetic field, before and after application of electric current pulse ($T = 3.77 \text{ K}$)

• Fig. 5 Electrical resistivity vs. temperature for 500Å carbon field, 300 to 900 K.

film

Fig. 6 Electrical resistivity vs. $T^{-1/4}$ for 500 Å carbon film, $T \leq 4.2$ K.