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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, 1970 to the present. The participating staff consisted of H. Weinstock (Associate Professor of Physics), C. Chau (Assistant Professor of Physics), and G. Kurz (Research Associate); the following graduate students: B Vis, S. Lu, M. Sayman, and S. Huang; and undergraduate students: D. Smith and J. Parpia.

I. Summary of Research Progress

A. Magneto-thermal Conductivity of Pyrolytic Graphite

The basal plane thermal conductivity of two highly oriented pyrolytic graphite samples has been measured from 0.36 to 4.2 K in several external magnetic fields along the direction of the heat flow. The results are shown in Fig. 1 and Fig. 2. The conductivity curve is strongly dependent upon the external magnetic field. This implies that the charge carriers contribute to the heat conduction. However, since it is found that the phonon-electron interaction in the samples is relatively weak, the observed thermal conductivity K is equal to the sum of the electronic thermal conductivity K_E and the lattice thermal conductivity K_L .

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$$K = K_L + K_E = AT^n + K_E, \quad (1)$$

where AT^n represents the lattice contribution to the heat flow. Only K_E depends on the external magnetic field H , so that the difference of any two thermal conductivity curves, $K(H_1) - K(H_2)$, is equal to the difference of their corresponding electronic component, $K_E(H_1) - K_E(H_2)$. These differences versus temperature are plotted in Fig. 3 and Fig. 4. The results clearly show that any set of $K_E(H_1) - K_E(H_2)$ is proportional to the absolute temperature T . Thus K_E may be expressed as

$$K_E = \gamma(H) T, \quad (2)$$

where $\gamma(H)$ is a function of the external magnetic field only. By extrapolation of the K/T versus T curve, it is possible to obtain γ for each external magnetic field.

In what follows the significance of the above results will be presented in terms of prevailing theoretical models.

The band structure of perfect graphite has been investigated in recent years (Ref. 1). A small interaction between second-nearest planes gives rise to a certain amount of band overlap at the Fermi energy, thus generating positive and negative charge carriers that are closely balanced in concentration. The free carrier densities of these carriers are low, about 10^{-4} /atom at room temperature, leading to essentially semi-metallic characteristics. In fact, an analysis of the basal plane properties of pyrolytic graphite can be based on a simple two-band model. Following the treatments of Drabble (Ref. 2), the ratio of the electronic thermal conductivity to the electrical conductivity can be expressed in terms of the energy overlap of the two bands and the temperature of the sample. For

highly oriented pyrolytic graphite and at temperatures below 4 K, the ratio is reduced to

$$K_E/\sigma T = L_0 = 2.45 \times 10^{-8} \text{ V}^2/\text{K}^2 \quad (3)$$

where σ is the electrical conductivity of the pyrolytic graphite and L_0 is the free electron Lorenz number. This result can be explained as follows. If the energy overlap of the two bands is large and the sample temperature is low, then the electrons in the overlap region can be treated as a highly degenerate electron gas. Thus the Wiedemann-Franz ratio will lead to the free electron Lorenz number. The electrical conductivity of pyrolytic graphite is found to be constant at temperatures below 4 K (Ref. 3). Therefore, χ should be equal to the product of σ and L_0 according to Eq. 2 and Eq. 3 as observed in the currently reported experiments.

The graphite crystallite boundaries limit the phonon mean free path at temperatures below 4 K. Thus, the lattice thermal conductivity is proportional to the crystallite size and its lattice specific heat. From this experiment, n in Eq. 1 is found to be 3 for $T < 1$ K and 2.5 for $1 \text{ K} < T < 4 \text{ K}$. This temperature dependence is in a good agreement with the temperature dependence of the specific heat according to Komatsu's "semi-continuum" lattice (Ref. 4 and 5). Furthermore, the crystallite size estimated from this experiment is about 25 microns, agreeing qualitatively with direct observation.

In conclusion, it has been found possible to separate the electronic thermal conductivity from the lattice thermal conductivity by means of an external magnetic field. This technique is essential to the future investigation of radiation produced defects in pyrolytic graphite. Currently,

work is being initiated on the thermal and electrical conductivity of additional graphite specimens, both pyrolytic and reactor grade; and arrangements are being made for neutron (and possibly heavy ion) irradiation. A complete exposition of the measurements and interpretation summarized above is presented in the M.S. Thesis of Miss S. Y. Lu, which accompanies this report.

B. Thermal Conductivity of Radiation Damaged MgO

As outlined in Progress Report No. 4, the first MgO crystals under investigation in this program showed a rather low thermal conductivity, plus a relatively sharp change in the thermal conductivity curve around 1 K. Tentatively, this behavior was believed due to the bubbles present in these crystals.

Further exchange of information with C. T. Butler of Oak Ridge National Laboratory (ORNL) revealed that the above mentioned crystals, although obtained from Oak Ridge, were not grown there. Instead, they had been purchased from a commercial source, W.&C. Spicer Ltd., England. The impurity level had been found to be higher than anticipated and in addition, the crystals of this batch showed a very strong infrared absorption due to OH^- impurity (Ref. 6). This is a bad omen as OH^- impurity in alkali halides is known to effect low temperature thermal conductivity markedly (Ref. 7).

An investigation of geometrical phonon scattering caused by bubbles, as well as by possible resonant scattering by molecular impurities (OH^- ions) is of considerable interest. However, this would not be within the main scope of the current program. Furthermore, no crystals varying in bubble

size and OH^- impurity concentration respectively were available. Hence, investigations on these (Spicer) crystals were discontinued.

To continue towards the aim of studying the influence of fast neutron irradiation on low temperature thermal conductivity, MgO crystals grown and kindly supplied by C. T. Butler at Oak Ridge were investigated. These crystals show a reasonably high thermal conductivity--see Fig. 5 for comparison of an ORNL crystal and a Spicer crystal. The thermal conductivity is roughly only $2/3$ less than that predicted by the simple Debye theory. However, a deviation from the theoretically predicted T^3 dependence is observed, the exponent found to be 2.7 rather than 3.0.

During the past year the CP-5 pile at ANL was shut down for a rehabilitation period. As a result, the fast neutron irradiation ($E > 1\text{MeV}$) was kindly carried out at ORNL with the kind help of Dr. C. Klabunde (although an inevitable time delay resulted from this inconvenience). To obtain a general feeling for the changes in conductivity produced by this type of irradiation, a total dose of 2×10^{18} neutrons/cm² was chosen. The irradiation temperature was about 50°C , i.e., an experimental situation which corresponds to the situation used in the earlier optical work done at ORNL (Ref. 8), and thus allowing an easy calculation of the number of defects generated. After the above stated irradiation the optical absorption spectrum revealed the expected bands at 250, 355, 574 and 975 nm respectively.

The results of the thermal conductivity measurements, both before and after irradiation, are presented in Fig. 6. Below 4 K, thermal conductivity is depressed with respect to that of the pure crystal by about an order of magnitude, and additionally a pronounced resonance type dip is also observed in the K vs T log-log plot.

Because of the large difference in thermal conductivity at 4 K an extension of these measurements to higher temperatures seemed to be desirable. R. O. Pohl of Cornell University kindly offered the opportunity to use one of his cryostats applicable for this higher temperature work. This opportunity was utilized, and the thermal conductivity of the irradiated and of a pure sample were measured at Cornell. Both sets of data (< 4 K and > 4 K) are plotted in Fig. 6. A second pronounced dip in conductivity is readily observed around the conductivity maximum at 25 K, the depression with respect to the pure crystal being more than a factor of 20. The data above 4 K obtained (by Dr. G. Kurz) at Cornell University were found to match those data obtained in the lower temperature range at IIT without qualification. Plans are now being made to modify the existing thermal conductivity cryostat to facilitate the taking of data at temperatures above 4 K at IIT.

Tentatively, one might ascribe the low temperature dip to geometrical scattering of colloids as proposed in Ref. 8. In that work, the authors propose that fast neutron irradiation produces F type centers and interstitials which at room temperature coagulate to form colloids. The analysis would, in that case, follow closely that used by R. A. Guenther and H. Weinstock (Ref. 9) for γ -irradiated KCl.

The dip in the vicinity of the maximum of the thermal conductivity curve might be ascribed to a resonant-like phonon scattering by F center type crystal defects. This tentative assignment is based on similar effects observed in alkali halides (Ref. 10).

It is clear that a more complete interpretation requires that a wider range of irradiations be employed. The first step in this continuing effort will be to vary

the total irradiation dose. Doses of 10^{17} and $10^{19} \frac{\text{neutrons}}{\text{cm}^2}$ are anticipated. For different concentrations of defects, the low temperature resonant-like phonon scattering should show no variation in the dip temperature assuming a constant cluster size. However, should a cluster size be a function of total dose or radiation intensity, a shift in the (temperature) position of the conductivity dip would be observed.

C. Thermal Conductivity of Cobalt Chloride Thiourea, $\text{CoCl}_2[(\text{NH}_2)_2\text{CS}]_4$, in Zero and Externally Applied Magnetic Fields

Although no new conductivity measurements have been carried out during the past year, previously obtained data have been subjected to further analysis as part of the effort to present a complete report of this effort for publication. A preliminary report (Ref. 11) has already been accepted for publication. In addition, with the recent completion of a helium dilution refrigerator in the laboratory, the earlier conductivity measurements will be extended downward in temperature by one more order of magnitude (to about 0.04 K) in order to provide a firmer basis for the interpretation of the current results.

In the continuing analysis of the thermal conductivity data, two important conclusions have been reached which lend additional weight to the major conclusions drawn previously. To reiterate these earlier conclusions, it was postulated that the thermal conductivity in zero external magnetic field below the Néel temperature (of 0.92 K) could be considered as the sum of a magnon conductivity (K_M) term and the usual phonon lattice conductivity (K_L), i.e.,

$$K = K_L + K_M$$

A quantitative analysis of the data was then made on this basis. The data obtained with heat flowing and an external 10 kG magnetic field in the [001] direction of sublattice magnetization, was found to match exactly (within a 2% experimental error) the lattice T^3 conductivity term obtained from the zero field data analysis. The one somewhat embarrassing point about this lattice term is that its magnitude (both above and below the Néel temperature) is about two orders below that predicted on the basis of simple Debye theory and the external dimensions of the specimen used.

Now it has been found (Ref. 12), however, that it is quite normal for crystals grown from solution to have crystallite grain boundaries on the order of tens of microns. This size is, in fact, compatible with the lattice conductivity observed. An effort is now being made to obtain verification of grain boundary size by optical microscopy.

An even more significant development involves the analysis of the K_M term in zero external field with the specific heat data obtained under similar conditions (Ref. 13). At temperatures below (and not in the immediate vicinity of) the Néel temperature, it was found that one could represent the magnon specific heat as

$$C_M \propto T^{4.86}$$

In the recent analysis of the thermal conductivity data, it was found that below about 0.6 K,

$$K_M \propto T^{1.8}$$

Using the usual argument for theoretical calculation of thermal conductivity,

$$K_M = 1/3 C_M v_M l_M$$

and assuming that the magnon group velocity (v_M) is temperature independent, one finds that the magnon mean free path

$$l_M \sim T^{-3}$$

This result is just what one would expect if the dominant scatterer of magnons is phonons.

In another effort to develop a clearer theoretical picture of the system under investigation, arrangements have been made with another laboratory to have infrared absorption measurements carried out at temperatures below the Néel temperature. These should yield an independent measure of the anisotropy exchange temperature (T_{AE}) which could then be related to the thermal conductivity measurements being planned at even lower temperatures with the new helium dilution refrigerator.

D. Nuclear Specific Heat of $UO_2Rb(NO_3)_3$

Earlier specific heat work on a ^{235}U enriched specimen of $UO_2Rb(NO_3)_3$ has now been implemented with measurements on a larger specimen containing normal (mostly ^{238}U) uranium.

The aim of this investigation is to extract that part of the specific heat data for the ^{235}U enriched specimen which is expected to yield a value for the nuclear electric quadrupole coupling constant. This constant would then be used to provide much needed information on the potential barrier in the ^{235}U nucleus.

At the present time, the normal uranium specimen has been returned to Dr. J. W. T. Dabbs at Oak Ridge National Laboratory for repacking as there

appears to be poor thermal contact between the compressed powder specimen and its gold plated copper container. Furthermore, this contact seems to have been deteriorating with time as evidenced by a recent experiment which had sought to improve and extend the earlier measurements.

The ^{235}U enriched specimen is currently being prepared for further measurement at temperatures below 1 K. Because of the high rate of self heating due to α particle emission, this has proven troublesome. The standard technique of applying a heat pulse to the isolated specimen could not be used, nor could one utilize the self heating in lieu of a heat pulse. Thus, a weak heat link method has been employed. This involves the application of a heat pulse to a specimen which is weakly linked to a thermal reservoir, in this case the ^3He cryostat, by means of a copper wire. A first attempt using this method yielded specific heat data down to 0.5 K which was of the correct order of magnitude, but whose scatter was too great to provide a meaningful extension to the higher temperature data obtained by the conventional technique. The attempt was useful, however, in providing information on the parameters required for more precise data. For example, shorter (but higher power) heat pulses must be used to satisfy the condition for simple analysis which requires this time to be short compared to the specimen-heat link relaxation time, a time which is a function of the heat capacity of the specimen and the thermal conduction of the heat link.

E. Optical Studies of Low Energy Radiation in Doped Alkali Halides

One member of the laboratory, Dr. G. Kurz, has collaborated with Dr. Sherman Susman of the Solid State Science Division at Argonne National Laboratory on a research program to study low energy radiation damage in alkali halides, i.e., the generation of vacancies and interstitials with incident photon energy as low as 5 ev (Ref. 14).

A hydride ion substitutionally placed on an anion lattice site of an alkali halide (U center) gives rise to a threefold degenerate, infrared-active local mode. Perturbations of the normal O_h symmetry can give rise to absorption band shifts and splittings that microscopically reflect the U defect interactions in the lattice (Ref. 15).

At 77 K photodissociation of hydroxide ions substitutionally incorporated in KCl yields U_2 centers and O^- ions:

It has been shown that these U_2 centers can be optically destroyed at 4.2 K according to:

In the current research effort, studies have been expanded to SH^- doped crystals. The results of the U_2 decomposition in this system agree with those obtained previously in OH^- doped crystals. This means that the O^- or S^- generated simultaneously with the U_2 centers, according to reaction (1), do not have an influence on the generation of U-H center pairs according to reaction (2).

U centers, produced by this intrinsic decomposition of U_2 centers, are most likely disturbed by nearby H centers as indicated by a broadening and a shift of the ultraviolet U band absorption. Ultraviolet measurements showed only that the U generation process was reversed by a sharp thermally activated step at 9.5 K and a second broader step between 40 and 60 K. The purpose of this program has been to study the microscopic details of the U-H

interaction by combined ultraviolet-infrared absorption spectrophotometry between 4.2 and 77 K.

High resolution spectra obtained during the past year have demonstrated that the formation of U by photodecomposition of U_2 and the subsequent thermally activated recombination is far more complicated than originally envisioned. The infrared spectra are identical for OH^- and SH^- doped specimens, and for a limited range of OH^- concentrations. This indicates that the perturbation on U is due to the H center and not to some other defect species. However, the infrared absorption band pattern of the photochemically generated U centers consists of at least twelve lines. Peak positions and band intensities suggest that the degeneracy removal is arising from H centers in 2nd and 4th coordination positions with unique orientations.

At 8.5 K the perturbed H center can tumble, but the Cl° cannot move interstitially through the lattice. While some of the bands vanish at this temperature, new bands appear. At 40 K, where the Cl° interstitial can move, there is at least a two step recombination occurring, probably dependent on U-H proximity and H orientation. Here, certain of the existing bands vanish, others increase in absorption intensity, while at least two remain uniquely unchanged up to at least 60 K.

Further experiments are required to interpret the observed perturbations on the local mode of the U center. It is currently assumed that the complex infrared spectra arise (1) from reduction of the site symmetry of the U center from O_h to C_{2v} and C_{4v} symmetries, and (2) from unique orientations of the H center relative to the U center. Bleaching into the long wavelength electronic transition of the H center at 5.6 K may yield an anisotropic distribution of H relative to U. Polarized infrared absorption measurements are planned.

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Fig. 1. Magneto-thermal conductivity of sample # 1.

Fig. 2. Magneto-thermal conductivity of sample # 2.

Fig. 3. Comparison between $K(H_1) - K(H_2)$ and $(\gamma(H_1) - \gamma(H_2))T$ for sample # 1.

Fig. 4. Comparison between $K(H_1) - K(H_2)$ and $(\gamma(H_1) - \gamma(H_2))T$ for sample # 2.

Fig. 5. Thermal conductivity vs. temperature for single crystals of MgO grown by W. & C. Spicer, Ltd., and C. T. Butler of Oak Ridge National Laboratory.

Fig. 6. Thermal conductivity vs. temperature for Oak Ridge grown MgO single crystal before and after irradiation of 2×10^{18} neutrons/cm² with energies greater than 1 MeV.

II. Graduate Student Progress

At the present time only two students are employed in the research activities of the laboratories.

Miss Shui-ying Lu has recently completed thesis research under the current project and has been awarded an M.S. degree in January, 1971. She is continuing both her education and research activities at IIT toward the fulfillment of requirements for a Ph.D. degree. She will pursue further the thermal and electrical conductivity measurements on pyrolytic graphite with the expressed purpose of using such measurements to detect the damage produced by neutron and carbon ion irradiation.

Mr. Benjamin Vis is an experienced junior scientist who carried out research at the Kammerlingh Onnes Laboratory in the Netherlands under Professor N. Poulis and at the University of Paris, France under Professor H. Benoit. He joined this laboratory in May, 1970, because of mutual interests in thermal and magnetic measurements of paramagnetic insulating solids, and the opportunity to earn a Ph.D. degree. Mr. Vis successfully passed the Ph.D. Comprehensive Examination in September, 1970, and now needs only to complete a successful thesis research project to be awarded the sought after degree. It is expected that this will be accomplished by September, 1972, or January, 1973.

It is anticipated that one or more graduate students will join the laboratory's research activities shortly when the results of the recently completed M.S. Comprehensive/Ph.D. Qualifying Examination are announced.

III. Progress in the Development of Laboratory Facilities

Construction and testing of a second cryogenic station utilizing helium dilution refrigeration has recently been completed. The first thermal conductivity measurements to be performed on it will be carried out shortly. Meanwhile, the station has already been used for some electrical conductivity measurements in the liquid helium four temperature range.

For the most part, the laboratory has now achieved the desired operational capability to carry out two simultaneous sets of thermal or electrical measurements at temperatures below 1 K - to 0.3 K for the helium three refrigeration system and to about 0.03 K for the helium dilution system. Only improved techniques for temperature measurement at the lowest temperatures and crystal growth need to be explored further.