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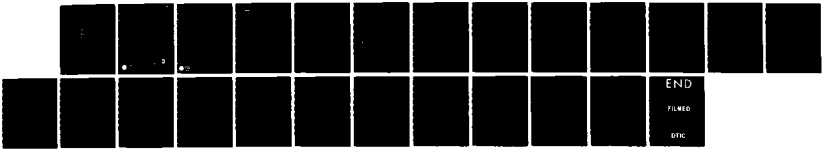

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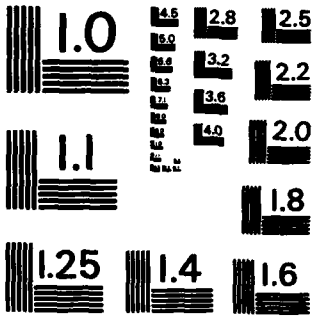

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Annual Report

AFOSR-TR- 84-1075

August 1, 1983 to August 1, 1984

HIGH SPECIFIC HEAT DIELECTRICS AND KAPITZA RESISTANCE AT DIELECTRIC BOUNDARIES

By

P. W. Eckels, W. N. Lawless,
J. H. Parker Jr. and B. R. Patton

Westinghouse Electric Corporation
Research and Development Center
Pittsburgh, Pennsylvania 15235

AFOSR Contract No. F49620-83-C-0129

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This program has two efforts: Kapitza and thermal properties studies. Two separate Kapitza conductance test facilities have been designed and fabricated for both solid-solid and for solid-liquid He II measurements. Preliminary data has been obtained for copper to ~~ICl~~ interface conductance and also for ~~KBr~~ and ~~LiF~~ thermal conductance to Helium II. For the latter two materials, the test dewars were designed to allow cleaving of the samples under liquid helium and subsequent irradiation of the cleaved surface thalium chloride

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zinc
cadmium
zinc chromium oxide
cadmium chromium oxide
cesium chloride

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1. Annual Report, Fundamental Physics Studies on High-Specific-Heat Dielectrics and Kapitza Resistance at Dielectric Boundaries

AFOSR Contract No. F49620-83-C-0129

P. W. Eckels, J. H. Parker Jr., W. N. Lawless and
B. R. Patton

2. ABSTRACT

This program has two efforts: Kapitza and thermal properties studies. Two separate Kapitza conductance test facilities have been designed and fabricated for both solid-solid and for solid-liquid He II measurements. Preliminary data has been obtained for copper to TlCl interface conductance and also for KBr and LiF thermal conductance to Helium II. For the latter two materials, the test dewars were designed to allow cleaving of the samples under liquid helium and subsequent irradiation of the cleaved surface with UV laser light. Preliminary experiments have been carried out on the effect of UV induced surface defect centers on the Kapitza conductance of KBr.

Thermal properties work has included the measurement of the specific heat and thermal conductivity of the $CdCr_2O_4$ and $ZnCr_2O_4$ spinels and of several CsCl structure heavy metal halides in the temperature range of 1.5 to 35K. The specific heat data for the spinels was analyzed in terms of both lattice phonons and magnetic contributions. The dependence of the spinels' thermal conductivity on magnetic fields up to 15T was studied and magnetocaloric data has been obtained. For both the Zn and Cd spinels, the latter results showed a paramagnetic behavior with demagnetization cooling and magnetization heating.

3. PROGRAM OBJECTIVES

- Carry out experimental studies on solid-solid and solid-liquid helium Kapitza conductance.
- Study the effect of surface defect centers and surface roughness on the solid-liquid helium Kapitza conductance for alkali halide materials.
- Analyze the Kapitza conductance data in terms of existing theoretical models.
- Obtain and analyzed specific heat data for spinel-columbite and alkali halide materials.
- Obtain and analyze thermal conductivity data for spinel-columbite and alkali halide materials.
- Study the effect of magnetic fields on both the specific heat and thermal conductivity.
- Develop theoretical models to interpret the above experimental results.

4. ACCOMPLISHMENTS

The long-range purpose of this program is to study insulating materials having potential as low-temperature superconducting wire insulations. The insulations are agglomerates and the thermal conductivity of agglomerates at low temperature is to a great extent controlled by the Kapitza conductance of the species' interface. Our approach to this study is to gain understanding of the material parameters affecting the Kapitza conductance. In describing our progress in this program we have reported the Kapitza studies and the other thermal properties work in separate sections starting with the Kapitza conductance studies.

4.1 Kapitza Studies

The Kapitza resistance at the interface of a superconductor surrounded by an insulator can become significant under several different conditions. For instance at the beginning of a transient heat pulse the effective heat transfer coefficient in a single material may be of the same size as the Kapitza conductance at its surface. Another condition when the Kapitza resistance can be the limiting factor in heat flow occurs in composite materials when a large number of particles of one material are mixed into another material. In this case the number of surface interfaces between the particles is so large that the total Kapitza resistance in the composite becomes large.

Both of these conditions occur for the materials presently being considered as a new generation of superconductor insulators and therefore there is a motivation for studying the Kapitza resistance of both solid-liquid and solid-solid interfaces in order to develop a basic physical understanding as well as to provide engineering numbers for design purposes.

At low temperatures, heat is transmitted by phonons and the limiting rate of transfer can be computed as the phonon radiation limit (PRL).[1] Various acoustic transmission theories predict phonon transmission rates that may be several orders of magnitude less than the PRL. Khalatnikov originated the first of these theories and others extended the acoustic mismatch theories (AM) attempting to explain the interface thermal resistance measured in the laboratory. Typically the measured values are found to lie nearer the PRL than the acoustic predictions. The anomalously large transmission is attributed to solid material effects by some researchers and to superfluid liquid effects by others. We have approached this study by concentrating upon the material effects and by evaluating the Kapitza conductance using heat transmission into superfluid helium and into solids.

Since the Kapitza conductance is a phonon transmission phenomena some experimenters have evaluated the conductance as the ratio of reflected to incident phonon energy from the material surface. The conductance is then presented as a fraction of the PRL. Of particular interest to this study is phonon data reported by Weber et al.[2] that indicates the absence of the anomalous Kapitza conductance in single crystals of NaF and LiF which were cleaved under liquid helium. Apparently contaminant and strain free smooth surfaces obtained by cleaving under liquid helium could be produced for study. We therefore proposed to cleave crystals under helium at 4.2K and irradiate the surface with UV laser light to form "F" or color centers that would be a well documented lattice defect introduced at known concentration levels. Knowing the detailed structure of the defects should enable the measured Kapitza conductance to be correlated with theory.

Kapitza measurements must be made under a variety of experimental conditions such as solid-to-solid and solid-to-liquid helium interfaces (and possibly solid-to-gaseous helium interfaces). The temperature conditions can vary from the critical point of liquid helium (5.25K) to below 1.5K and with pressures up to at least 2.26 atm. (the critical pressure of He^4).

4.1.1 Kapitza Status: Westinghouse

After an extensive literature search, an optical dewar was prepared in which a single crystal of KBr, KI or LiF could be cleaved under He II. Considerable effort was expended in developing a solid sample support system that had acceptable heat leak characteristics and which was compatible with cooldown contraction. The present design surrounds a right circular cylinder crystal with a teflon canister that uniformly shrinks onto the crystal at low temperature. The diameter of the cylinder is 1 cm and the length is about 2 cm. Support is provided for the teflon by the metal dewar walls. Carbon resistors are used as temperature sensors. They are placed in holes drilled into the crystals. Copper leads to the thermometers are coiled inside the holes in the crystals and actually make the thermal contact to the crystal. The thermometers are calibrated during each run at each experimental point using the saturation temperature-pressure relation for helium. A heater (wire wound) is applied to the recessed end of the crystal with GE lacquer. Heat fluxes in excess of 1 W/cm^2 can be generated by the heater. Two carbon resistors are positioned along the sample to provide redundancy and establish the temperature gradient in the sample. A third carbon resistor indicates the bath temperature.

Initial tests were performed with copper to prove the experimental apparatus. These tests yielded Kapitza values that have been found by others. Subsequently KI, KBr and LiF crystals were tested. The measured values for all of the crystals cleaved under liquid helium were 75% of the PRL or higher. We have not been able to reproduce the phonon propagation results of Weber et al. It should be noted that Wyatt,[3] in a postscript to his paper in the 1980 NATO Summer Workshop on Nonequilibrium Phonons, indicates that the reflection technique may not give any useful information on the anomalous transmission of phonons across interfaces. We appear to have confirmed that speculation. Although we have not been able to complete the original objectives of this program at this point, establishing that there is no correlation between phonon propagation experiments and heat transfer experiments is a very important contribution and

must be carefully confirmed before publishing these results. Another aspect of these results is that they tend to diminish the importance attributed to surface contamination as a mechanism contributing to the anomalous Kapitza conductance. Since cleaving under liquid helium certainly prevents surface contamination from oxygen, oils, water and other gases, the anomalous conductance present in the cleaved samples must be the result of existing roughness, internal strains or dislocations. We have found the dislocation and impurity density of commercial crystals in the literature[4] and they seem to be inconsequential. We therefore plan to pursue the surface roughness aspect of the as-cleaved surface.

Preliminary investigation has led us to a recent paper by N. S. Shiren[5] which describes a model relating Kapitza conductance to a statistical description of surface roughness. The complete and detailed model has not, as yet, been published but we have contacted Shiren and he has no reservations about helping us analyze our experimental results. Our plans are to work with cleaved LiF crystals. We would first measure the Kapitza conductance for a specific sample. Then the sample would be sectioned and the surface geometry (roughness) would be sampled using transmission electron microscopy. Using a number of sections, a statistical characterization of the surface would be obtained. Discussions with our material characterization group at the Westinghouse R&D Center have indicated that a resolution of about 10A can be expected. The surface roughness that is obtained would be put into Shiren's model and its prediction would be compared with the experimental Kapitza values.

4.1.2 Kapitza Status: CeramPhysics

A probe has been designed and built to handle a broad range of conditions. The cold end of the probe is isolated from a surrounding helium bath by a vacuum can sealed with an indium o-ring. Inside the vacuum can is a helium subpot (a separate reservoir of liquid helium) which can be filled by opening a valve between the subpot and the helium bath. Hanging from the bottom of the subpot is an adiabatic shield which surrounds the experimental sample which is also thermally anchored to the subpot. For solid-to-solid Kapitza measurements the subpot acts as a

thermal reservoir and samples can be easily attached and anchored thermally to it. There is also a small port in the bottom of the subpot which is normally sealed using an indium o-ring seal. When making a solid-to-liquid helium Kapitza measurements, this seal can be removed and a small helium chamber (with the solid material to be measured sealed into it) can be attached.

Temperature is controlled two ways. The helium subpot is attached to a large external vacuum pump which can lower the subpot temperature by pumping on the liquid. The pumping can be done through a special valve which can maintain a constant vapor pressure (and therefore a constant temperature) within the subpot. Over most of the range 1.5K to 4.2K, this temperature can be controlled within millikelvins over periods of hours. There is also a separate electronic temperature controller which provides current to a heater on the subpot. This controller is also capable of controlling temperatures to within millikelvins for long time periods.

The correct way to make Kapitza measurements on a solid-solid interface is to put two thermometers on each material, measure the temperature difference across each pair of thermometers and then extrapolate the temperature gradient in each material to the interface in order to determine the temperature drop across the interface. This all occurs when one material is thermally anchored to the subpot reservoir and a heater is attached at the opposite (free) end of the other material. The four thermometers have been chosen to be Allen-Bradley carbon thermometers (nominal 220Ω at room temperature). During each cooldown they are calibrated versus a germanium resistance standard which has in turn been directly calibrated against another germanium calibrated at the National Bureau of Standards.

At this point in time, the probe has been designed, machined, and assembled along with the auxiliary pumping lines and the electrical switching and control systems. A preliminary test run was completed to test the system and to learn the proper experimental techniques. The probe and other equipment performed flawlessly.

The preliminary test was a solid-to-solid interface between a sample of thallium chloride and copper. Preliminary results give the Kapitza resistance as

$$R_K = DT^{-n}$$

where n = 3.52. D is dependent upon the actual contact surface area between the two samples and has not yet been accurately determined. Both n and D appear to be consistent with the range of values measured by other experimenters on other interfaces. A full report on these measurements will be written shortly.

The next step is to refine the measurement techniques and then prepare various interfaces for study. A solid-to-liquid helium interface will be tested shortly. The only problem yet to solve with this measurement is finding a leak-tight seal between the solid sample and the helium space, but this should be no real problem. At least one interface will be selected shortly for measurements in high magnetic fields at the National Magnet Laboratory at MIT. The other interfaces will be investigated under various experimental conditions while concentrating on relating the measurements to the basic theories about Kapitza resistance.

4.2 Thermal Properties

The purpose of this part of the program is to determine and understand the thermal properties (specific heat and thermal conductivity) of a recently formulated group of compounds having potential as superconducting wire insulation in the future.

4.2.1 Spinel Studies

The spinels $CdCr_2O_4$ (T_c = 8.0K) and $ZnCr_2O_4$ (T_c = 10.5K) can be reproducibly formed in ceramic bodies only in the presence of the columbite mineralizers $CdNb_2O_6$ and $ZnNb_2O_6$, respectively, and the resulting materials have enormous specific heat maxima, making them technologically

important. The ceramic samples studied here had spinel: columbite ratios 9:1, so that the spinel phases constituted about 85 vol. %.

The first study undertaken was to measure high-precision specific heat data, 1.5 to 35K, on both the 9:1 ceramics and the columbite mineralizers (formed separately). The data for both columbites could be accurately described by Schottky and Einstein terms added to the Debye background, and these fittings were employed to correct the 9:1 ceramics' data to obtain the specific heats of the spinel phases.

The specific heats of the spinels were analyzed at the higher temperatures ($T > T_c$) according to a Schottky model which gave an excellent representation of the data. The resulting Debye temperatures for $CdCr_2O_4$ and $ZnCr_2O_4$(420.1 and 463.0K, respectively) agree very well with predictions of the Lindemann relation (414 and 469K, respectively).

At the lower temperatures ($T < T_c$), the specific heat data for both spinels also follow a Schottky model very well, suggesting an additional magnetic transition below 1.5K. However, the Debye temperatures resulting from these fittings are suspiciously small (101 and 162K, respectively). This huge discrepancy in Θ_D's is strong evidence for antiferrimagnetic spin waves which contribute a T^3 term to the specific heat, as does the Debye term. Adopting the Θ_D's from the high temperature region, these spin-wave contributions can be separated and we find that

$$CdCr_2O_4: \quad J's/C_a^{1/3} = 5.943 \times 10^{-16} \text{ erg}$$

$$ZnCr_2O_4: \quad J's/C_a^{1/3} = 9.651 \times 10^{-16} \text{ erg} \qquad (1)$$

where C_a depends on the lattice geometry.

These fitting studies allow us to estimate the magnetic entropy of these spinels associated with the specific heat maxima at 8.0 and 10.5K in $CdCr_2O_4$ and $ZnCr_2O_4$, respectively. The specific heat of each spinel is decomposed into the following contributions: (1) the Debye background

(θ_D = 420 and 463K, respectively), (2) antiferrimagnetic T^3 spin waves; (3) Schottky term above T_c, (4) Schottky contribution below T_c, and (5) the magnetic contribution causing the maxima at 8.0 and 10.5K. The lattice contribution is assumed to be terms (1) and (4) above, the remaining terms being the magnetic contribution. Using the fitting parameters for contributions (1) through (4) and the total specific heat, we find the following magnetic entropies:

$$CdCr_2O_4: \quad S_m/R = 2.340$$

$$ZnCr_2O_4: \quad S_m/R = 1.434 \tag{2}$$

The next study undertaken involved measuring specific heat data at small temperature intervals (~ 10 mK) in the neighborhood of the specific heat peaks in $CdCr_2O_4$ and $ZnCr_2O_4$. This was done using a "drift" method wherein the drift rate of the sample temperature, dT/de, was measured, and a long-time-constant thermal link was employed. In this fashion, about 100 specific heat points were measured in the range $T_c \pm 1K$. This method also yielded very accurate T_c - values,

$$CdCr_2O_4: \quad T_c = 7.958K$$

$$ZnCr_2O_4: \quad T_c = 10.637K \tag{3}$$

These data were analyzed according to the renormalization group theory of critical exponents. Satisfactory fits to the data were obtained, and the critical exponents for both spinels are $\alpha = 3.2$. These are very large critical exponents and are difficult to reconcile according to renormalization group theory. It is suggested that critical phenomena may not be involved in these spinels.

These drift experiments also established that there is no latent heat associated with the specific heat maxima in either $CdCr_2O_4$ or $ZnCr_2O_4$.

A literature survey was undertaken for these spinels. The enthalpies of formation of the spinels have been reported, as have the catelytic properties of $ZnCr_2O_4$. The X-ray lattice constants and densities of the spinels have been reported by the NBS, and brief mention has been made of a first-order transition in $ZnCr_2O_4$ at 12.8K (contrary to our findings). No papers appear in the literature concerning the physics of these spinels as addressed in this program.

The next experimental studies undertaken were devoted to measuring the thermal conductivities (K) of these spinels (since the columbite phases constitute only ~ 15 vol. %, the thermal conductivities of the 9:1 ceramics can be taken as those of the spinel phases). It was found that in both spinels there is a considerable jump in K at a temperature slightly below T_c, and this is a significant effect (e.g., in $ZnCr_2O_4$, K doubles in the jump).

Pursuing these results further, thermal conductivities were measured in intense magnetic fields (up to 15T) in the neighborhood of the K-jumps. For $CdCr_2O_4$ an H-field suppresses K linearly, $(\partial K/\partial H)_T = 4.73 \times 10^{-3}$ mW cm^{-1} K^{-1} T^{-1}), whereas in $ZnCr_2O_4$ K is independent of H. It is estimated that at H ≈ 50T the jump in K for $CdCr_2O_4$ would be eliminated.

The last experimental studies undertaken to date were devoted to the magnetocaloric properties of these spinels at 3.2 and 4.5K (i.e., at temperatures well below T_c). Both spinels display adiabatic demagnetization cooling and magnetization heating, and there are no detectable hysteretic effects. The temperature changes are very large (e.g., $\Delta T \simeq 1K$ at 9T at 3.2K) considering how large the specific heats are at these temperatures, and the ΔT's for $ZnCr_2O_4$ are consistently larger than for $CdCr_2O_4$. The magnetization of both spinels was measured at 4.2K up to 7T, and it was found that both spinels act as linear paramagnets. The magnetization of $CdCr_2O_4$ is about three times larger than that of $ZnCr_2O_4$.

The experimental evidence to date indicates that both spinels undergo a second-order transition to an antiferrimagnetic state at T_c, and that there are several degrees of magnetic freedom remaining below these transitions.

4.2.2 Theoretical Studies – Spinels

Theoretical studies have concentrated on the new spinels $CdCr_2O_4$ and $ZnCr_2O_4$ which heretofore have not been investigated.

The physics literature on the neighboring spinels such as $CdCr_2S_4$, $ZnCr_2Se_4$, etc. was examined to see if general trends could be identified, and the following conclusions were drawn: Based on bonding anisotropies it is clear that $CdCr_2O_4$ and $ZnCr_2O_4$ are normal, face-centered-cubic spinels (i.e., as opposed to inverse spinels), which helps explain their magnetic transition occurring at low temperatures. For ferrimagnetic ordering one expects T_c ~ 100K, whereas for antiferrimagnetic ordering, T_c ~ 20K, and this general observation reinforces the experimental finding of antiferrimagnetic spin waves. These antiferrimagnetic spin lattices in normal spinels are highly frustrated because for symmetry reasons not all the spins can order. This observation qualitatively explains why so many degrees of freedom exist below T_c as evidenced in the experimental magnetocaloric data. A Jahn-Teller distortion may be important in explaining the jump in the thermal conductivity. These general considerations allow a construction of spin diagrams for these spinels.

A first principles Hamiltonian was constructed that characterizes the interaction of the spins with each other, the lattice, and the external field, and from this model Hamiltonian the relevant order parameters were extracted to obtain a theory of a phenomenological Ginsberg-Landau nature. The Cr^{3+} - Cr^{3+} superexchange occurs <u>via</u> the Cd (or Zn) ion, and this 90° superexchange is a weak interaction.

A free-energy functional is constructed in terms of the order parameters which are the sublattice magnetizations, and this functional is analyzed for the mean-field solutions. A <u>linear</u> magnetization is obtained above and below T_c; however, the susceptibility is predicted to have a strong temperature dependence below T_c, and this comes from a renormalized ferrimagnetic mode below T_c which couples to the antiferrimagnetic mode.

The specific heat is obtained from the free energy in the mean-field approximation although the results are not necessarily accurate

unless the material has long-range interactions. The jump in the specific heat (C) at the transition is obtained, and the H-field dependence of C below T_c is explicitly related to a coupling coefficient between two different order parameters.

4.2.3 Cesium and Thallous Halides

Specific heat and thermal conductivity data, 1.7 to 30K, were measured on single crystals of the CsCℓ-structure, heavy-metal halides (i.e., CsBr, CsI, TℓC , TℓBr, and TℓI), including thermal conductivity measurements on thin crystal bars of CsBr, TℓC , and TℓBr. Effective Debye temperatures are in generally good agreement with deformable-dipole lattice dynamics theories. Evidence for a hydroxyl content (~ 10^{20} cm^{-3}) in CsBr and CsI is inferred from a Schottky term at the lowest temperatures and the known zero-field splitting in alkali halides. This term is absent in the (less hygroscopic) thallous salts.

All of these salts display strong maxima in C/T^3 describable by Einstein oscillators. The Einstein frequencies can be interpreted as the first rapid rise in the density of states, and comparisons with available neutron scattering data are excellent.

The thermal conductivities of all these salts show maxima at ~ 5K, and for CsBr a T^3 boundary scattering behavior is seen that scales with the crystal dimension. For TℓCℓ and TℓBr, however, the thermal conductivity is independent of the crystal dimension, and this is interpreted as due to phonon scattering from a mosaic structure within these crystals. The heat-carrying modes in these crystals are identified using a Peierls analysis relating the experimental thermal data.

A large paper on these studies has been accepted for publication in The Physical Review.

4.2.4 Future Plans

The work on the thermal properties of the CsCℓ-structure salts is essentially completed and will be published shortly. Some peculiar H-field effects in CsI have been seen, and these will be pursued at the National Magnet Laboratory as time and opportunity allow.

The experimental studies of the $CdCr_2O_4$ and $ZnCr_2O_4$ spinels have largely been completed this first year, and the impetus will shift in the second year to theoretical studies. There remain, however, some rich experimental areas to pursue further: (1) H-field dependence of K at various temperature and (2) magnetocaloric studies at temperatures near T_c. Finally, the area of critical exponents may be revisited, since CeramPhysics has recently developed the computer-interface capability to perform high-precision drift experiments resulting in even smaller temperatures intervals near T_c.

5. PUBLICATIONS

"Specific Heat and Thermal Conductivity Measurements on Cesium and Thallous Halide Crystals at Low Temperature," W. N. Lawless, accepted for publication in the Physical Review.

6. PERSONNEL

Westinghouse: P. W. Eckels, Co-Principal Investigator
J. H. Parker Jr.
A. Patterson

CeramPhysics: W. N. Lawless, Co-Principal Investigator
C. F. Clark

Ohio State: B. R. Patton

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