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THERMAL AND ULTRASONIC TRANSPORT PROPERTIES OF DIELECTRIC AND PIEZOELECTRIC SOLIDS

FINAL REPORT

Paul G. Klemens
and
Frederick P. Lipschultz

December 14, 1976

U.S. Army Research Office-Durham

Grant No. DAHC04-74-G-0068

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

This Final report describes measurements of the thermal conductivity of single crystal alumina from 1 to 70 K and the effect of electron irradiation, and of the thermal conductivity and ultrasonic attenuation of lithium niobate. Point defect scattering of phonons was also studied through lattice thermal conductivity of copper-germanium. Theory of thermal conductivity of crystals at high temperatures was extended in terms of four-phonon processes, optical modes and thermal expansion. A surface wave transducer can be made by → over

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20. Abstract (cont.)

periodically modulating a piezoelectric surface; attempts to make such a device are described.

Final Report on

"Thermal and Ultrasonic Transport Properties of Dielectric and Piezoelectric Solids"

U.S. Army Research Office-Durham

Grant No. DAHC04-74-G-0068

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I. Introduction

The main objective of the program was to improve the understanding of thermal conduction and ultrasonic attenuation of dielectric and peizoelectric crystals. These properties are both controlled by the interaction of thermal phonons with crystal defects and with each other. However, the phonon relaxation times which enter into the theory of these two properties are not defined in the same manner. Therefore these two properties, while related, are not simply proportional to each other. In order to test the basic theoretical concepts, it was proposed to measure both the thermal conductivity and the ultrasonic attenuation on the same material, and to monitor changes in these properties due to physical defects. It was also proposed to extend the theories of phonon transport and phonon interaction processes, so as to improve the understanding of thermal conduction and ultrasonic attenuation.

The experiments were made principally on two substances: single crystal alumina (sapphire) and lithium niobate. In the case of lithium niobate, both the thermal conductivity and the ultrasonic attenuation were measured on the same material-differently shaped specimens cut from neighboring positions in the same boule. Lithium niobate, while optically and ultrasonically clear, proved to contain a surprisingly high density of sub-microscopic defects, which became evident in the low-temperature thermal conductivity and the "residual" ultrasonic attenuation at low temperatures. Also, these properties seemed to be related, scaling according to the difference in the phonon frequency by the same frequency dependence of the phonon mean free path as had been derived from each of these properties individually. However, so far it has not been possible to identify the defects responsible. Both properties were found to be insensitive to gamma ray irradiation, possibly because of the high prior concentration of defects.

The thermal conductivity of sapphire was sensitive to radiation damage by electrons, probably as a result of the conversion of valence state of transition metal impurities.

The detailed analysis of the thermal conductivity of sapphire was made difficult, because its high temperature conductivity does not agree with simple theory. The theory at high temperatures was therefore re-examined. It had been widely believed that four-phonon processes caused the observed departures from the inverse temperature dependence, which had originally been ascribed by Peierls to cubic anharmonicities. The magnitude of the thermal resistance due to four-phonon processes was estimated theoretically, and it was found that four-phonon processes cannot account for the observed departures. These departures seem to be, in most cases, due to the thermal expansion of the solid. It was also found that thermal expansion can give a good account of the departures of the electrical resistivity of gold from a linear temperature dependence.

The thermal conductivity of dielectric solids at ordinary and high temperatures is reduced by neutron irradiation; this reduction is largely due to point defects. In order to better understand the scattering of phonons by point defects, in particular the role played by the distortion of the surrounding lattice around the point defect, it is helpful to study the lattice thermal conductivity of metallic alloys, where the solute concentration is known and where X-ray data gives information about the strength of the distortion. The lattice thermal conductivity of copper-germanium was therefore measured over a wide temperature range. Preliminary information indicated that this system behaves anomalously. It was found that point defect scattering of phonons is much weaker than had been expected from X-ray data.

II. Thermal Conductivity of Sapphire

Measurements of the thermal conductivity of nominally pure sapphire were made from 1K to 70K, in the "as received" state, after electron irradiation, and after subsequent annealing. Uniform penetration of the electrons was achieved by rotating the sample during irradiation.(1) The peak conductivity of the "as received" sample was 70 $W\text{-}cm^{-1} - K^{-1}$, indicating a small prior concentration of point defects. This was also borne out by a lower exponent in the exponential "Umklapp" region of thermal conductivity above the peak temperature of 34K. Electron irradiation (1-2 x 10^6 Rad of 1 Mev electrons) reduced the thermal conductivity below 40K by 20 to 25%. The conductivity recovered almost completely after annealing 24 hours at 600°C in a helium atmosphere. Electron irradiation thus produces effects very similar to those produced by gamma irradiation.(2) Pre-existing transition metal impurities seem to convert their valence state from one in which coupling to the lattice is normal to one in which coupling is very strong and of resonance character; this leads to a strong reduction in the low temperature thermal conductivity,(2,3) though the reduction at higher temperatures is expected to be smaller. Annealing returns the impurity ion to its original valence state, and the low temperature thermal conductivity recovers.

III. Thermal Conductivity of Lithium Niobate

Similar measurements were made on lithium niobate ($LiNbO_3$), but the results were quite different. Firstly, the thermal conductivity indicated a large concentration of sub-microscopic defects in the "as received" state, even though the crystal was of highest quality acoustically, and was quite clear optically. The thermal conductivity showed a broad peak at about 15K of less than 1.2 $W\text{-}cm^{-1}\text{-}K^{-1}$. This is well below the value expected from the Casimir limit, where the phonon mean free path is governed by the specimen diameter. Although the phonon mean free path was found to increase with decreasing temperature, it had still not reached the Casimir limit at about 1K.

Secondly, there was no measurable effect on the thermal conductivity by 1-2 x 10^6 Rad of gamma irradiation in a cobalt cell. This exposure should have been equivalent to the electron irradiation of the sapphire experiment. This negative result may be ascribed to the large number of defects in the "as received" crystal, but the radiation-induced defects, if any, could also have annealed out at room temperature, before the sample was inserted into the thermal conductivity cryostat. Therefore, electron spin resonance spectra were obtained at 77 and 300 K, and optical absorption spectra at 300 K, both before and after X-ray irradiation, to see if one could detect either pre-existing or radiation-induced centers. All spectra were essentially featureless. It thus appears that the radiation-induced conversion of impurities to strong scatterers of phonons, which is such a prominent feature of the sapphire system, does not occur in lithium niobate or is at least weak. Nevertheless, there must be a substantial concentration of defects in lithium niobate, as evidenced by the low temperature thermal conductivity.

The thermal conductivity around 70K appears to link up well with previous measurements at ordinary temperatures.(4)

IV. Ultrasonic Attenuation in Lithium Niobate

The attenuation of ultrasonic compressional waves was measured at 300 and 700 MHz over a continuous temperature range from 5 to 300 K. Ideally the ultrasonic measurements should have been conducted on the same sample as the thermal conductivity measurement. Conflicting geometrical requirements made this impossible. The thermal and ultrasonic specimens were therefore cut from adjacent positions in the same boule.

At 700 MHz, the attenuation decreases from 0.225 dB/cm at room temperature to a low-temperature residual value of 5.1×10^{-2} dB/cm. It was also noticed that the residual attenuation increased slightly on thermal cycling between low temperatures and room temperatures. Lithium niobate is very brittle: it is possible that thermal stresses produce small scattering domains which lead to this slight increase in ultrasonic attenuation. This also raises the question whether some of the thermal resistance may be due to the same cause. However, we believe that most of the thermal resistance at low temperatures arises from pre-existing defects.

Although the thermal phonons which contribute to heat conduction at liquid helium temperatures have frequencies higher than the ultrasonic frequency by a factor of order 100, their mean free path seems to be limited by the same scattering mechanism. The thermal conductivity mean free path varies with frequency a little faster than the inverse first power, and this is also the frequency dependence of the inverse of the ultrasonic attenuation. Furthermore, the same frequency dependence brings the magnitude of the two quantities into agreement, over a gap in relevant frequencies of a factor 100. This would suggest a common scattering mechanism, possibly dislocations. Unfortunately, a self-consistent model has not been found. Not only is the required dislocation density too high, but dislocations of that density could not scatter independently of each other at ultrasonic frequencies. The magnitudes of the attenuation and of the thermal conductivity mean free path suggest a common mechanism of scattering, but the failure to find a self-consistent model may imply that the agreement between these two quantities could be fortuitous.

V. Transducers for Acoustic Surface Waves

In theory it is possible to generate acoustic surface waves from an electromagnetic signal not only by modulating the electric field configuration on a piezoelectric surface, as in the conventional interdigital transducers, but also by using a uniform electric field but modulating the piezoelectric parameters on the surface with the periodicity of the desired acoustic surface wave. While this principle was proposed in a patent disclosure,(5) the physical realization of such a device has proved to be not straightforward, and will require further work.

Initially, and in order to confirm the principle, strips of piezoelectric material, half a wave-length wide, were laid down on an aluminum flat, with the piezoelectric direction alternatingly inverted. These strips had been cut simply from a compression wave quartz transducer. A generating and detecting array were made, and enclosed in a simple parallel plate capacitor. Surface waves at 3.3 MHz were transmitted between them. The surface wave character was established by appropriate tests. This particular arrangement demonstrated the principle, but cannot be scaled down to the frequencies of device applications.

In order to realize a device with modulated piezoelectric properties, two methods can be used in principle. It is known that one can reverse the sense of the piezoelectric tensor in deposited films by interposing a chemically similar but non-piezoelectric film between two piezoelectric films(6) - e.g. PbS between hexagonal CdS. By a suitable sequence of masking, etching and depositions one can lay down, on top of a uniform layer, strips of a second layer with reversed piezoelectric tensor. This sequence has been described,(5) but we lack the necessary deposition equipment to carry it out.

An alternative method, which would not achieve the same filling factor, aims to produce strips of piezoelectric material separated by piezoelectrically inactive strips. Such inactive strips can be made from piezoelectrically active material by radiation damage, either by locally changing the structure, or by making the material locally conducting, thus reducing the electric field. This second method introduces some losses by necessity; this is an inherent disadvantage. Ideally the radiation damage in the alternate strips should extend to a depth of the order of the wavelength of the surface wave.

An attempt was made to realize this second type of transducer by bombarding a lithium niobate surface with 1 Mev protons through a suitable mask of strips and slits. We failed to obtain a working transducer pair, perhaps because the depth of damage was too small. It is planned to repeat the experiment with 2 Mev protons, which have now become available to us. However, it may be that the losses in the damaged region will always outweigh the generation due to the modulation of the piezoelectric properties. Further work is being done to understand the modulation process.

VI. Theory of Lattice Thermal Conductivity

The thermal conductivity of sapphire at temperatures above that of the peak (34K) was analyzed in terms of intrinsic three-phonon interactions (Umklapp processes) and point defect scattering. The exponent in the exponential temperature dependence of the Umklapp regime was shown to depend on the point defect concentration. However, it proved difficult to link these conductivities at intermediate temperatures to the high temperature values in a consistent manner, because the thermal resistivity at high temperatures varies faster with temperature than the linear temperature dependence of the Peierls theory. This is so not only for alumina, but also for a number of refractory oxides.(7) The theory of the thermal conductivity at high temperatures was therefore studied.

A number of authors had analyzed the high temperature thermal resistivity into terms proportional to T, the absolute temperature, and proportional to T^2, ascribing the former to three-phonon and the latter to four-phonon interactions. In order to test this explanation, the magnitude of the T^2 component was calculated, using the quartic anharmonicity and the cubic anharmonicity to second order.(8,9) The T^2 component due to four-phonon processes was found to be an order of magnitude smaller than the observed T^2 component. In order to account for this observed component one must consider thermal expansion. The T dependence theoretically predicted for the thermal resistance due to three-phonon processes was based on a constant volume of the crystal. Because the thermal conductivity is sensitive to dilatation,(10) thermal expansion gives rise to a T^2 component of the thermal resistivity which seems to account for the observations on polycrystalline aggregates. High-temperature measurements on single crystals are reliable only in the case of semiconductors; in these cases there seems to be an additional departure from theory which has been attributed to a small group of low-frequency longitudinal phonons with very large mean free path.(11) This component of the conductivity cannot occur in polycrystalline solids.

The role of optical phonons in three-phonon interactions and in the thermal resistance process was also investigated.(9,12)

VII. Electrical Resistivity of Gold

Other high-temperature conduction properties of solids are also influenced by thermal expansion. Departures of the electrical resistivity of simple metals from a linear temperature dependence were attributed to thermal expansion already by Mott and Jones.(13) Using recently compiled data on the electrical resistivity of gold, together with thermal expansion data and the known pressure dependence of the electrical resistivity at room temperatures, a very good fit was obtained for the temperature dependence of the electrical resistivity from room temperature to almost the melting point, leaving a small component of electrical resistivity below the melting point to be attributed to thermal vacancies.(14) This analysis also provides a reliable base to which low temperature conductivities can be compared, showing that around 100K there is a component due to electron-phonon Umklapp processes which progressively increases with temperature.

VIII. Lattice Thermal Conductivity of Copper-Germanium

The thermal conductivity of dielectric solids is reduced by neutron irradiation. This reduction is due in part to extended defects, but at room temperatures and above it is due mainly to point defects stabilized by defect aggregates.(15) To fully understand the effect of such point defects, it is necessary to predict the scattering of phonons by the distortional strain field around the defect. The lattice thermal conductivity of simple substitutional metallic alloys provides a particularly effective test of this theory, since the nature and concentration of the point defects are well known. The system copper-germanium is of particular interest, because the solute atom has almost the same mass as the parent atom, and because the distortional strain field is large, so that phonon scattering is essentially due to the distortion.

The lattice thermal conductivity of two copper-germanium alloys (4.5 and 9 at % Ge) was measured from 1 to 70 K, annealed as well as cold-worked. Around its maximum, i.e. around 30 K, the lattice conductivity is very sensitive to solute scattering of phonons. The scattering cross-section thus deduced was compared to the cross-section calculated from the distortional strain field. The latter had been estimated from the change of lattice spacing on alloying. In contrast to other copper alloys, the observed scattering cross-section was weaker than had been expected from the X-ray data. It appears that the discrepancy is caused by the fact that the distortion is less than expected, because the Cottrell atmospheres around the dislocations in the cold-worked specimens were also too weak, but consistent with the distortion estimated from the phonon scattering cross-section of the solute atoms. It is not clear why the distortion is less than the apparent distortion of the X-ray data. A preliminary account of this work has been published,(16) and a full account is being prepared.

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