

## THERMAL CONDUCTIVITY IN HIGH PURITY MATERIALS

A.K. Sreedhar and N. Chaudhuri

Defence Science Centre, Metcalfe House, Delhi 110054, INDIA

**Abstract** - The role of impurities in the thermal conduction by phonons in semiconductors is reviewed. Thermal transport properties are profoundly influenced by the presence of such impurities and defects, especially in pure materials and at low temperatures. A study of thermal conductivity in solids gives valuable information about the impurity as well as its state of aggregation. Some typical results in semiconductors are reviewed and discussed.

### INTRODUCTION

Trace impurities have pronounced effects on the transport properties of solids. As is well known, in semiconductors an impurity of the order of one part in  $10^{11}$  -  $10^{12}$  can have measureable effects on the electrical properties of a crystal and electrical measurements such as Hall effect have been used to obtain information about impurities in a semiconductor. Impurities have also profound effects on the thermal transport properties of these materials. Thermal conductivity measurements in a highly pure insulating crystal containing trace impurities can give valuable information about the nature of the "defect state" they bring about in the crystal lattice. In this short review, some of the typical measurements of thermal conductivity in insulating materials will be discussed from the point of view of the information that these provide on the "defect state".

### THERMAL CONDUCTIVITY IN INSULATING SOLIDS

Thermal conduction can be considered as transport of energy by "excitations" in the solid. Phenomenologically one can write

$$K = \frac{1}{3} \sum C v l$$

based on the kinetic theory model, where  $K$  is the thermal conductivity,  $C$  is the specific heat of the excitation per unit volume of the crystal,  $v$  is their characteristic mean velocity and  $l$  the mean free path. The summation is taken over all possible excitations. These can be phonons, electrons, photons (at high temperatures) etc. In semiconductors and insulating crystals at low temperatures, the phonons contribute mainly to the thermal conductivity and the scattering of phonons by various defects such as impurities, point defects, crystal or grain boundaries etc., limits the mean free path. The above formula assumes that thermodynamic equilibrium is restored after each scattering. We can define a relaxation time for each scattering process by

$$l = v \tau$$

When more than one scattering process plays a role simultaneously

$$\tau^{-1} = \sum_i \tau_i^{-1}$$

The importance of thermal conductivity measurements rests on the fact that each scattering process has in general a different temperature variation and enables one to estimate  $\tau$  for well known scattering processes by

measuring thermal conductivity as a function of temperature.

The various scattering processes that are of importance in the thermal conductivity of a semiconductor are listed in Table 1.

TABLE 1. Relaxation time for phonon scattering at low temperatures

Scattering processes	Relaxation time
Boundary	$\tau_b^{-1} = g v / l$
Point defects	$\tau_{pd}^{-1} = (\delta^3 \Gamma / 4\pi v^3) \omega^4$
Phonon-electron	
Ziman	$\tau_{ep}^{-1} = \frac{\epsilon^2 m^{*3} v}{4\pi \hbar^4 d} \left\{ \frac{kT}{\frac{1}{2} m^{*2} v^2} \right\} \left\{ \frac{\hbar\omega}{kT} - \ln W \right\}$
Keyes (modified by Griffin and Carruthers)	$\tau_p^{-1} = \text{Const. } \epsilon_u^2 n_{ex} (4\Delta)^2 \times \omega^4 / (1 + \tau_0 \omega^2) \times [\hbar^2 \omega^2 - (4\Delta)^2]^{-2}$

where,

- $g$  = numerical factor to take into account diffuse scattering
- $l$  = equivalent sample diameter
- $v$  = velocity of phonons
- $\delta^3$  = molecular volume
- $\Gamma$  = function of impurity concentration, mass difference, force constant and nearest neighbour distance
- $\omega$  = phonon frequency
- $\epsilon$  = phonon-electron interaction constant (deformation potential)
- $m^*$  = effective mass of electron
- $d$  = density
- $W$  = function of Fermi energy, temperature and phonon frequency
- $\epsilon_u$  = shear deformation potential
- $n_{ex}$  = concentration of uncompensated donor electrons
- $4\Delta$  = splitting of ground state impurity energy level (chemical shift)
- $\tau_0$  = averaged Bohr radius of hydrogen like donor state

Figure 1. shows schematically the variation of thermal conductivity as a function of temperature and regions where a specific scattering process or processes are of importance in limiting the thermal conductivity. Since the effect of controlled trace impurities can be observed best in crystals of semiconductors and alkali halides, which can be obtained in a high state of purity, further discussion will be confined to these materials only.

In these materials the thermal conduction at low temperatures ( $T \ll \theta$  Debye) is mainly due to phonons. The main scattering processes which limit the conductivity are (i) boundary scattering & (ii) point defect scattering. The boundary scattering leads to the variation of thermal conductivity proportional to the lattice specific heat and hence proportional to  $T^3$ . The mean free path is of the order of the crystal dimensions as per Casimir, (Ref. 1). This has been observed in the thermal conductivity of high purity InSb (Ref. 2), GaAs (Ref. 3), isotopically enriched Ge (Ref. 4), LiF (Ref. 5) etc. For example, in the case of isotopically enriched germanium,  $^{74}\text{Ge}$ , the experimental value for the mean free path is about 1.80 mm., as

compared with the value of 1.57 mm., calculated from the cross sectional area of the sample.

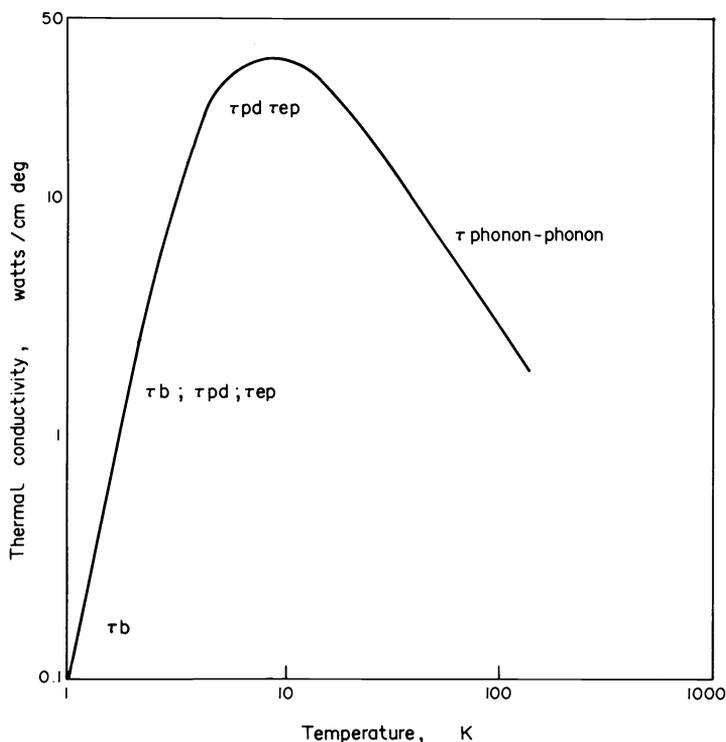


Fig. 1. Variation of phonon thermal conductivity as a function of temperature.

However, the agreement between theory and experiment is not universally applicable for all semiconductors. For example, in naturally occurring germanium the low temperature behaviour indicates that a more accurate treatment of the combined behaviour of boundary and mass defect scattering is required. For Te-doped GaAs (Ref. 6), for example, the boundary scattering mean free path agrees fairly well with theory. However, for Cr-doped GaAs this is not so. There is an order of magnitude difference between the observed and theoretical results. This has been explained on the basis of the presence of second phase precipitates (of CrAs) in the GaAs crystal which reduce the mean free path. In general, pure semiconductors and mostly those with n-type impurities show fair agreement with the theory in the boundary scattering region. Semiconductors with p-type impurities show larger decrease in thermal conductivity at low temperatures than those with n-type impurities.

This decrease of thermal conductivity below the maximum is substantial even for small doping concentrations. The temperature variation is also not proportional to  $T^3$  at lowest temperatures as per Casimir's theory. Ge and GaSb show this type of anomalous behaviour at low temperatures.

Ziman's theory (Ref. 7) of scattering of phonons by electrons in the impurity band and Pyle's theory (Ref. 8) of hopping electrons and Keyes' theory (Ref. 9) of strain sensitivity of impurity energy levels have been used to account for these anomalous results. Good agreement with experiment is obtained on the basis of Keyes' theory and its extension by Griffin and Carruthers (Ref. 10), who have taken into account the possibility of resonant scattering between energy levels of the impurity atom and the phonons. Such resonant scattering between phonons and low lying energy levels due to other origins such as Jahn-Teller effect have been observed in alkali halides by Pohl (Ref. 11) and in MgO by Challis (Ref. 12).

Mn doped GaAs shows a depression in the thermal conductivity indicating resonant scattering of phonons by impurity levels. Holland (Ref. 3) has explained this on the basis of Keyes theory mentioned above. Cr-doped GaAs (Ref. 6) also shows a resonant scattering. This has been interpreted as indicative of a possible Jahn-Teller effect. However, more extensive work on thermal conductivity in semiconductors with dopings of transition metal impurities is required to account for the detailed behaviour of phonon transport at low temperatures.

The thermal conductivity in semiconductors reaches a peak value at around 10 K due to the different temperature variations of the various scattering processes of importance at that temperature region, viz., boundary, Keyes' electron-phonon interaction mechanism, point defect scattering and phonon-phonon scattering. The height of the peak or the maximum in thermal conductivity is an indication of the purity of the material as the peak value is sensitive to point defect scattering. Thus, it is observed that isotopically enriched Ge (Ref. 4), has a peak value of about three times the value for a similar natural Ge crystal.

#### CONCLUSION

An impurity being an "excitation" in an otherwise perfect crystal will cause profound effects in the crystal lattice. Some of these are strain fields, distortion of the local symmetry due to Jahn-Teller effect, existence of low lying impurity energy levels, some of which are affected by magnetic fields. There is also the possibility of micro-segregation of impurity complexes.

All these have profound effects on the transport of phonons in the crystal. Thus a measurement of thermal conductivity of semiconductors and other non-metallic crystals with dopings of specific impurities will give a wealth of information about the nature of impurity in an otherwise perfect lattice.

#### REFERENCES

1. H.B.G. Casimir, Physica **5**, 495 (1938).
2. M.G. Holland, Phys. Rev. **134**, A 471 (1964).
3. M.G. Holland, Physics of Semiconductors, (Proc. Int. Conf. Phys. Semicond. Paris 1964), Dunod, Paris and Academic Press, New York (1964).
4. T.H. Geballe and G.W. Hull, Low Temperature Physics and Chemistry, (Proc. Int. Conf. Low Temp. Phys. and Chem. Wisconsin 1957), The University of Wisconsin Press, Madison (1958).
5. R. Berman, P.T. Nettle, F.W. Sheard, A.N. Spencer, R.W.H. Stevens and J.M. Ziman, Proc. Roy. Soc. A **253**, 403 (1959).
6. N. Chaudhuri, R.S. Wadhwa, Phoola Tikur and A.K. Sreedhar, Phys. Rev. B **8**, 4668 (1973).
7. J.M. Ziman, Phil. Mag. **1**, 191 (1956).
8. I.C. Pyle, Phil. Mag. **6**, 609 (1961).
9. R.W. Keyes, Phys. Rev. **122**, 1171 (1961).
10. A. Griffin, and P. Carruthers, Phys. Rev. **131**, 1976 (1963).
11. R.O. Pohl and C.T. Walker, Phys. Rev. **131**, 1443 (1963).
12. I.T. Challis, M. de Goer, K. Guckelsberger and G.A. Slack, Proc. Roy. Soc. A **330**, 29 (1972).