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Thermal Conductivity of Magnesium Stannide

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The thermal conductivity of the semiconductor Mg_2Sn has been determined in the temperature range 80 to 700°K from measurements of the thermal diffusivity. At low temperatures the thermal conduction is entirely lattice conduction, as shown by our earlier measurements from 4 to 300°K. At higher temperatures, however, our results show that bipolar-electronic conduction (diffusion and recombination of electron-hole pairs) becomes important and actually equals the lattice conduction at 700°K. The difference between our measured thermal conductivity and the lattice thermal conductivity is in good quantitative agreement with the calculated bipolar-electronic thermal conductivity, and this agreement gives strong support to the theory of bipolar conduction in semiconductors.

Key Words: Bipolar conductivity, lattice conductivity, magnesium stannide, semiconductor, thermal conductivity, thermal diffusivity.

1. Introduction

Mg_2Sn is a II-IV compound semiconductor with the antiferrofluorite structure and is a member of the Mg_2X family of compounds where X can be Si, Ge, Sn or Pb. Elastic constants and calculated lattice vibration frequencies have been reported by Davis et al. [1]¹. The electrical properties of Mg_2Sn have been reported by Winkler [2] and others [3-5]. Umeda [6] and Crossman [7] report that the electronic structure of Mg_2Sn consists of ellipsoids along the [100] directions. Busch and Schneider [8] have reported thermal conductivity data on Mg_2Sn from 77 to 400°K. Recently, Martin and Danielson [9] measured the thermal conductivity of several Mg_2Sn samples from 4.2 to 300°K. These results indicated that below 300°K lattice conduction is completely dominant in Mg_2Sn ; the thermal conductivity is proportional to T^{-1} from 150 to 275°K. Above room temperature Mg_2Sn is completely intrinsic and the lattice conductivity is small (0.075 W/cm-deg at 300°K); hence, the electronic contribution should be a large part of the total thermal conductivity. Therefore, we have extended our measurements by a thermal diffusivity technique to 700°K in order to determine the electronic thermal conductivity of Mg_2Sn .

2. Experimental Procedure

The single crystal sample was grown by a modified Bridgman technique. The sample was grown from 99.999% purity tin and from magnesium distilled under high vacuum in this Laboratory from 99.99% purity starting material. The sample was n-type. Figure 1 shows the electrical resistivity data taken on the diffusivity sample before and after the thermal diffusivity measurements. Figure 1 also shows the Hall coefficient of the sample that was measured prior to the thermal diffusivity measurements. The Hall data indicates that the sample contained approximately $2.5 \times 10^{16} \text{ cm}^{-3}$ uncompensated donors before the thermal diffusivity measurements were made. The change in the electrical resistivity data after the diffusivity measurements were completed indicates that the donor concentration increased to about $3 \times 10^{16} \text{ cm}^{-3}$. The sample dimensions were 4.30 x 4.24 x 20mm.

We have developed new instrumentation so that thermal diffusivity data may be taken on short samples by our finite difference method. The new data recording apparatus is similar to our old gear [10] except that Astrodata model 120R amplifiers are used for D. C. amplification and a four trace oscilloscope is used to record the temperature versus time curves. Typical pulse times are 5 sec.

¹Figures in brackets indicate the literature references at the end of this paper.

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The sample was mounted in a sample holder which contained Pt versus Pt-10% Rh and Cu versus constantan thermocouples for temperature measurements above and below room temperature. Three Cu wires were spark welded to the sample at distances of 5, 7.5 and 10mm from the resistance wire heater wound on one end of the sample. A fourth Cu wire was spark welded to the opposite end of the sample for use as a reference lead. The three Cu versus Mg_2Sn versus Cu reference differential thermocouples were used to measure the three temperature versus time curves in the sample. The data were taken in a cryostat-furnace which could cover the temperature range 80 to 700°K.

3. Results

Our thermal diffusivity results are shown in fig. 2. The curve represents the best fit to the data and was used to calculate thermal conductivity values. The thermal conductivity was calculated from the smoothed thermal diffusivity, the x-ray density [11] of 3.592 gm/cm³ and the specific heat. The specific heat values of Jelinek et al. [12] were used between 80 and 300°K, and the specific heat values of Gschneider [13] were used between 300 and 700°K. The thermal conductivity curve is shown in fig. 3 along with our low temperature thermal conductivity data and the earlier data of Busch and Schneider [8]. Between 80 and 300°K our new data is in good agreement with our old thermal conductivity data and with the data of Busch and Schneider.

4. Discussion

In a semiconductor, heat may be carried by the lattice (phonons) and by the charge carriers (electrons and holes). The total thermal conductivity, K , can be expressed as a sum of the lattice conductivity, K_L , and the electronic thermal conductivity, K_e :

$$K = K_e + K_L. \quad (1)$$

In order to determine K_e we must subtract K_L from the total thermal conductivity. From 150 to 275°K the thermal conductivity of Mg_2Sn goes as T^{-1} which is characteristic of three phonon scattering.

Since the Debye temperature is about 200°K and three phonon scattering processes will continue to dominate the lattice conductivity at higher temperatures, we expect the T^{-1} temperature dependence to continue. Mg_2Sn becomes completely intrinsic near 300°K so we expect the electronic thermal conductivity to become important above 300°K. Figure 4 shows a plot of the thermal resistivity of our sample (K^{-1}) versus T . The line represents the $K^{-1} \sim T$ extrapolation of our data. We will use this line as our high temperature extrapolation of the lattice conductivity.

The electronic thermal conductivity, K_e , was obtained by subtracting the lattice conductivity, K_L , from the total thermal conductivity. At 700°K, $K_e \approx K_L$.

If we assume acoustic mode scattering of both the electrons and holes, the electronic thermal conductivity can be expressed as

$$K_e = \left(\frac{k}{e}\right)^2 \left\{ 2 + \frac{(4 + \Delta E/kT)^2 n_{ph}}{(bn + p)^2} \right\} \sigma T. \quad (2)$$

In eq(2) k is Boltzmann's constant, e is the electronic charge, ΔE is the energy gap at temperature T , b is the mobility ratio μ_e/μ_h , n and p are the electron and hole concentrations, and σ is the electrical conductivity. The first term expresses the ordinary Wiedemann-Franz law for a non-degenerate material. The second term represents the transport of the recombination energy of the electrons and holes and is called the bipolar contribution to the electronic thermal conductivity. The bipolar term is usually much larger than the Wiedemann-Franz term because $\Delta E/kT \gg 1$.

Winkler [2] found an energy gap of $(0.36 - 3 \times 10^{-4}T)$ eV for Mg_2Sn . The ratio, b , of the electron mobility to the hole mobility in the intrinsic range was found to be 1.20-1.25 by Lipson and Kahan [14] and 1.23 by Blunt et al. [3]. For the calculation of K_e we shall use $b = 1.23$. In the intrinsic region ($T > 300^\circ K$ for Mg_2Sn) $n=p$. The solid line in figure 5 shows the electronic thermal conductivity calculated from eq 2. The electrical conductivity measured on our sample was used in the calculation along with the energy gap of Winkler [2] and $b = 1.23$. The calculated and measured electronic thermal conductivities agree to within 3mW/cm-deg which is about 5% of the total thermal conductivity.

5. Summary

The thermal conductivity of the semiconductor Mg_2Sn has been determined by thermal diffusivity measurements between 80 and 700°K. The data between 80 and 300°K are in good agreement with our direct thermal conductivity results. From 150-275°K, the thermal conductivity goes as T^{-1} which is characteristic of high temperature lattice conductivity. The electronic thermal conductivity which was determined by subtracting the extrapolated lattice conductivity from the measured thermal conductivity is in good agreement with the calculated electronic thermal conductivity. At 700°K the electronic thermal conductivity was equal to the lattice thermal conductivity.

6. References

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Figure Captions

- Figure 1. The Hall coefficient and electrical resistivity of our thermal diffusivity sample that were measured before the thermal diffusivity data were taken and the electrical resistivity that was measured after the thermal diffusivity was measured is shown.
- Figure 2. The thermal diffusivity of Mg_2Sn .
- Figure 3. The smoothed thermal conductivity calculated from the thermal diffusivity is shown with the results of our earlier thermal conductivity measurements.
- Figure 4. The points show the smoothed thermal resistivity of our sample. The straight line represents our estimate of the lattice conductivity.
- Figure 5. The curve represents the calculated electronic thermal conductivity. The points represent the difference between our total thermal conductivity and the estimated lattice conductivity.