Phonon Conductivity of Mg_2Sn

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(Received 14 August 1969)

The two-mode conduction of thermal energy as proposed by Holland has been used to explain the temperature dependence of the phonon conductivity of Mg_2Sn in the temperature range 4–300°K, especially the change in slope at about 80°K. The elastic part of Kwok's expression for the resonance-scattering relaxation rate for phonons is shown to account for the magnitude near the conductivity maximum. The present work also shows that practically all the transport of thermal energy is due to transverse phonon.

I. INTRODUCTION

RECENTLY, thermal conductivity of Mg_2Sn has been studied by Martin and Danielson[1] in the temperature range 4–300°K. In order to account for the observed values of the phonon conductivity at different temperatures, they considered phonon-phonon scattering, isotope scattering, boundary scattering, and scattering by bound donor electrons. Martin and Danielson could explain their data only up to 50°K (see Figs. 4 and 5 of Ref. 1), where the phonon-conductivity–versus–temperature curve shows a change in slope which persists up to room temperature. Martin and Danielson remarked that phonon conductivity beyond 150°K shows a T^{-1} dependence but did not make any attempt to explain their data beyond about 80°K, although it may be remarked that it would not have been possible for them to explain the change in slope as well as the phonon conductivity data beyond 50°K on the basis of their expressions of the combined relaxation time τ_c in the framework of Callaway's theory.[2] It may be seen from Figs. 4 and 5 of Ref. 1 that the discrepancy between theory and experiment increases continuously with the increase in temperature beyond 50°K.

The above difficulties are, however, quite satisfactorily removed and it is possible to explain the phonon conductivity results in the entire temperature range 4–300°K, including the change in the slope which occurs at about 80°K, if one considers the two-mode conduction first proposed by Holland. Here one has to consider separately contributions of longitudinal phonons and transverse phonons which act as carriers of thermal energy. Although Holland's approach involves more computational labor, it is more general in the sense that one makes a distinction between longitudinal phonons and transverse phonons. The calculations are more realistic in that the actual dispersion curves along certain symmetry directions are used in obtaining the frequency and temperature dependence of $\tau_{3\text{-phonon}}^{-1}$ for transverse phonons, in determining the average phonon velocities for the different branches, and also in determining the limits of the conductivity integral.

It may also be remarked that Martin and Danielson have used ω^4 dependence for the resonant scattering of phonons,[3] which is not valid when $\hbar\omega \gg 4\Delta$ and $k_BT \gg 4\Delta$. Here the difficulty lies in that the value of 4Δ, which is the energy difference between the donor electron ground state and the first higher-energy state, is not known. Martin and Danielson could obtain good agreement between theory and experiment for the values of the phonon conductivity near the maximum which lies below 50°K by considering $4\Delta = 5\times10^{-4}$ eV. If we consider this value a reasonable approximation to the correct value, then the temperature at which resonance occurs is $T_r \sim \frac{1}{6}(4\Delta/k_B) \cong 1$°K. Thus the temperature range of interest in the present work, 4–300°K, corresponds to $\hbar\omega \gg 4\Delta$ and $k_BT \gg 4\Delta$. Recently, Kwok[4] has derived expressions for phonon attenuation due to the resonant scattering of phonons by considering both elastic and inelastic scattering of phonons off the ground state as well as off the next higher-energy state. For $\hbar\omega \gg 4\Delta$ and $k_BT \gg 4\Delta$, it can be shown that the resonant-scattering relaxation rate $\tau_r^{-1} \propto \omega^2$. Thus we have preferred to use $\tau_r^{-1} \propto \omega^2$ rather than $\tau_r^{-1} \propto \omega^4$, which is valid for $\hbar\omega \ll 4\Delta$ and $k_BT \ll 4\Delta$.

The aim of the present paper is to explain the phonon conductivity results of Mg_2Sn in the temperature range 4–300°K as well as the change in slope in the K-versus-T curve at about 80°K. The basis of the explanation is sought in the two-mode conduction approach proposed by Holland.[5] This also enables us to investigate the role of transverse phonons in the thermal resistance of Mg_2Sn. For the resonant scattering of phonons by bound donor electrons we have considered Kwok's theory which leads to $\tau_r^{-1} \propto \omega^2$ for the present temperature range of interest.

[1] J. J. Martin and G. C. Danielson, Phys. Rev. **166**, 879 (1968).
[2] J. Callaway, Phys. Rev. **113**, 1046 (1959).
[3] A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).
[4] P. C. Kwok, Phys. Rev. **149**, 666 (1966).
[5] M. G. Holland, Phys. Rev. **132**, 2461 (1963).

Lattice vibration spectra as obtained by Davies *et al.*[6] for Mg_2Sn have been used in determining the limits of integration as well as the phonon velocities for the different regions of the curves.

II. THEORY

The lattice thermal conductivity[5] K is separated into two parts: (1) K_T, which is the contribution of transverse phonons, and (2) K_L, which is the contribution of longitudinal phonons. K is then given by

$$K=K_L+K_T, \tag{1}$$

where

$$K_T=\tfrac{2}{3}T^3\int_0^{\theta_T/T} C_T\frac{x^4e^x(e^x-1)^{-2}\,dx}{\tau_T^{-1}}$$

and

$$K_L=\tfrac{1}{3}T^3\int_0^{\theta_L/T} C_L\frac{x^4e^x(e^x-1)^{-2}\,dx}{\tau_L^{-1}}, \tag{2}$$

$$x=\frac{\hbar\omega}{K_BT},\quad \theta_i=\frac{\hbar\omega_i}{K_B},\quad C_i=\frac{K_B}{2\pi^2v_i}\left(\frac{K_B}{\hbar}\right)^2, \tag{3}$$

and $i=L$ and T.

As has been discussed in detail by Holland,[5] one can calculate the contribution of transverse phonons to phonon conductivity by separating the corresponding conductivity integral into two parts: (1) contribution of phonons whose frequencies range from 0 to ω_1, and (2) contribution of phonons with frequencies from ω_1 to ω_2. Here ω_1 is the frequency where UK processes start and ω_2 is the highest TA mode frequency. The lattice thermal conductivity due to transverse phonons, therefore, is given by

$$K_T=K_{T_1}+K_{T_2}$$
$$=\tfrac{2}{3}T^3\int_0^{\theta_1/T}\frac{C_{T_1}x^4e^x(e^x-1)^{-2}\,dx}{\tau_{T_1}^{-1}}+\int_0^{\theta_2/T}\frac{C_{T_2}x^4e^x(e^x-1)^{-2}\,dx}{\tau_{T_2}^{-1}}, \tag{4}$$

where C_{T_1} and C_{T_2} can be calculated from the phonon spectrum of the substance. Lattice vibrational spectra and elastic constants for Mg_2Sn have been reported by Davies *et al.*[6]

The relaxation times used are

$$\tau_L^{-1}=v/L+A\omega^4+B_L\omega^2T^3,$$
$$\tau_{T_1}^{-1}=v/L+A\omega^4+B_{T_1}\omega T^4,$$

and

$$\tau_{T_2}^{-1}=\frac{v}{L}+A\omega^4+\frac{B_{T_2}\omega^2}{\sinh(\hbar\omega/K_BT)}, \tag{5}$$

where $v/L=\tau_B^{-1}$ is the inverse of the boundary scattering relaxation time, v is the average phonon velocity, L is the effective Casimir[7] length which is known in terms of the dimensions of the specimen, $A\omega^4=\tau_{\rm pt}^{-1}$ corresponds to scattering of phonons by point defects such as isotopes for which Rayleigh scattering is assumed, and A is the point-defect scattering strength which is known accurately for mass-difference scattering such as isotopes from Klemens's formula.[8] $B_L\omega^2T^3=\tau_{\rm pp}^{-1}$[9] is the inverse of the phonon-phonon scattering relaxation time for longitudinal phonons, where it is assumed that this form takes care of both normal and umklapp processes, B_L is the scattering strength which is treated as an adjustable parameter, $B_{T_1}\omega T^4=(\tau_{\rm pp}^{-1})_{T,\omega<\omega_1}$ is the phonon-phonon scattering relaxation time for transverse phonons for $\omega<\omega_1$, where it is assumed that umklapp processes are absent for $\omega<\omega_1$,

$$\frac{B_{T_2}\omega^2}{\sinh(\hbar\omega/K_BT)}=(\tau_{pp}^{-1})_{U,\omega_1<\omega<\omega_2},$$

derived first by Holland for Ge, is the inverse of the phonon-phonon scattering relaxation time for umklapp processes for transverse phonons in the region $\omega_1<\omega<\omega_2$, and it is assumed that normal phonon-phonon scattering processes make negligible contribution in this region. The scattering strengths B_{T_1} and B_{T_2} for transverse phonons are treated as adjustable parameters. The average sound velocity v is given by

$$v^{-1}=\tfrac{1}{3}(2v_T^{-1}+v_L^{-1}). \tag{6}$$

The characteristic length L is given by $2R$ for a specimen of circular cross section of radius $2R$ and is equal to $1.12S^{1/2}$ for a rectangular cross section of area S. The point-defect scattering strength for mass-difference scattering, according to Klemens,[8] is given by

$$A=\frac{V_0}{4\pi v^3}\sum_i f_i\left(1-\frac{m_i}{\bar m}\right)^2, \tag{7}$$

where V_0 is the atomic volume, m_i is the mass of the ith species of the atom, and $\bar m$ is the average atomic mass.

III. SCATTERING OF PHONONS BY DONOR ELECTRONS

From the measurements of the Hall coefficient and electrical resistivity, Martin and Danielson[1] have determined the donor concentration in Mg_2Sn, which is approximately 2×10^{16} cm^{-3} for the sample 2a. The

[6] L. C. Davies *et al.*, J. Phys. Chem. Solids, **28**, 439 (1967).

[7] H. B. G. Casimir, Physica **5**, 595 (1938).

[8] P. G. Klemens, Proc. Phys. Soc. (London), **A68**, 1113 (1955).

[9] Recently, G. L. Gutherie [Phys. Rev. **152**, 801 (1966)] has shown that for longitudinal phonons in the high-temperature region, one should use $\tau_{3\text{-phonon}}^{-1}\alpha T$ rather than $\tau_{3\text{-phonon}}^{-1}\alpha T^3$. However, the longitudinal contribution to phonon conductivity remains small even if one uses $\tau_{3\text{-phonon}}^{-1}\alpha T$. Hence, for the sake of using a minimum number of adjustable parameters, we have used $\tau_{3\text{-phonon}}^{-1}\alpha T^3$ for longitudinal phonons both for the low-temperature and high-temperature regions.

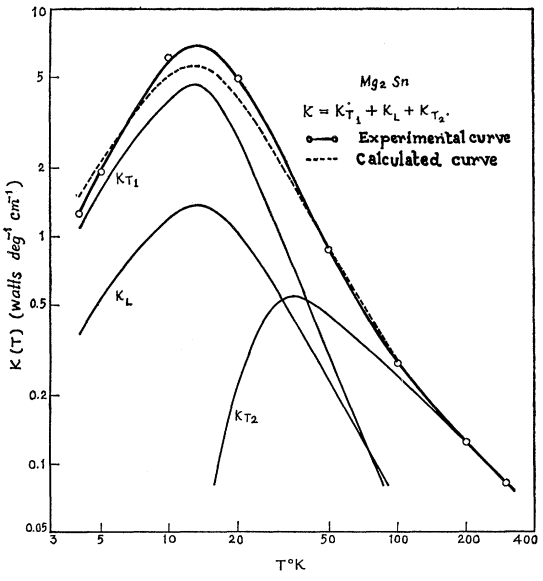

FIG. 1. Thermal conductivity of Mg_2Sn. K_{T_1} is the contribution of transverse phonons of frequencies lying between 0 and ω_1, K_{T_2} is the contribution of transverse phonons of frequencies lying between ω_1 and ω_2, K_L is the contribution of longitudinal phonons, and K is the total thermal conductivity. The calculations of $\tau_{q\lambda}^{-1}$ have been done using Eqs. (8). The solid line through the plotted points is the experimental curve, and the dashed line is the calculated curve.

donor levels are approximately 1×10^{-3} eV below the conduction band. Umeda[10] has reported the electronic structure of Mg_2Sn and showed that one can apply the many-valley conduction-band results of Ge and Si to this lattice.

The elastic scattering of phonons by bound donor electrons due to virtual electronic transitions may be written symbolically as

$$\hbar\omega_{q\lambda}+(\text{ground state})\rightleftharpoons(\text{int.})\rightleftharpoons\hbar\omega_{q'\lambda'}+(\text{ground state}),$$
$$\hbar\omega_{q\lambda}+(\text{excited state})\rightleftharpoons(\text{int.})\rightleftharpoons\hbar\omega_{q'\lambda'}+(\text{excited state}),$$

where the states mentioned in parentheses are the hydrogenic states of a shallow donor atom. Here $\omega_{q\lambda}$ is the phonon frequency for the phonon $(\mathbf{q},\lambda)$ and $\omega_{q\lambda}=\omega_{q'\lambda'}$ for the elastic scattering of phonons.

It has been found in the present investigation that elastic phonon scattering processes alone account for the observed thermal resistance. Considering only the elastic scattering part, one can simplify the expressions for the resonant-scattering relaxation rate as obtained by Kwok[4] ($\hbar\omega_{q\lambda}\neq4\Delta$). The simplified expressions can be written as

$$\tau_{q\lambda}^{-1}=HF^2(q)[f_0(T)(\hbar\omega_{q\lambda}/4\Delta)^2+f(T)]\omega_{q\lambda}^2,$$
$$\text{for } \hbar\omega_{q\lambda}\ll4\Delta \quad (8a)$$
$$=HF^2(q)[f_0(T)+f(T)]\omega_{q\lambda}^2, \text{ for } \hbar\omega_{q\lambda}\gg4\Delta. \quad (8b)$$

Here H is proportional to the fourth power of the shear deformation potential and the ignorance about the details of the band structure is lumped into the proportionality factor H. Here $f_0(T)$ and $f(T)$ represent the population of the ground state and the next higher-energy state, respectively. 4Δ is the energy separation between the ground state and the next higher-energy state. The form factor $F(q)$ is given by

$$F(q)\cong(1+r_0^2\omega_{q\lambda}^2/4C_\lambda^2)^{-2}, \quad (9)$$

where r_0 is the average radius of the donor orbit. The values of 4Δ and r_0 used in the present calculation of the resonant-scattering relaxation rate on the basis of Kwok's theory are the same as those used by Martin and Danielson.

The first term in Eq. (8a) (for $\hbar\omega_{q\lambda}\ll4\Delta$), representing the elastic scattering of phonons off the ground state, is proportional to the population of this state and to the fourth power of phonon frequency. The second term in Eq. (8a), corresponding to the elastic scattering of phonons off the next higher-energy state, is proportional to the population of this state and the square of the phonon frequency. Equation (8b), representing the elastic scattering of phonons off the ground and the excited state (both contribute almost equally when $\hbar\omega_{q\lambda}\gg4\Delta$), is proportional to the population of the state considered and to the square of the phonon frequency.

IV. COMPARISON OF THEORY AND EXPERIMENT

Martin and Danielson have studied the thermal conductivity of Mg_2Sn at different temperatures in the range 4–300°K. Here, we have calculated the thermal conductivity of the sample 2a with Casimir lengths $L=3.45$ mm. We have used a two-mode conduction model for the thermal conductivity. The various parameters used in the calculation of the phonon conductivity are given in Table I. Figure 1 shows the comparison between theory and experiment for the temperature dependence of the phonon conductivity of Mg_2Sn.

The following conclusions may be drawn from the present work:

TABLE I. (a) Parameters used for $\tau_{q\lambda}^{-1}$ [$H_{L,T}$ are the adjustable parameters used in Eqs. (8) (Kwok)]. (b) Parameters used for lattice thermal conductivity.

(a)

$v=3.59\times10^5$ cm/sec	$\rho=3.592$ g/cm³
$H_L=10^5$ deg^{-2} sec^{-1}	$H_T=1.5\times10^5$ deg^{-2} sec^{-1}
$4\Delta=5\times10^{-4}$ eV	$r_0=40$ Å
$N_{ex}=2.4\times10^{16}$ cm^{-3}	

(b)

$\omega_1=1.1842\times10^{13}$ sec	$v_{T_1}=3.1926\times10^5$ cm/sec
$\omega_2=1.5526\times10^{13}$ sec	$v_{T_2}=1.1651\times10^5$ cm/sec
$\omega_3=3.1842\times10^{13}$ sec	$v_L=4.7895\times10^5$ cm/sec
$\tau_b^{-1}=1.0406\times10^6$ sec^{-1}	
$A=5.6\times10^{-44}$ sec³	$B_L=2.92\times10^{-22}$ sec deg^{-3}
$B_{T_1}=2.29\times10^{-11}$ deg^{-4}	$B_{T_2}=5.84\times10^{-17}$ sec

[10] T. Umeda, J. Phys. Soc. Japan **19**, 2052 (1964).

(1) The assumption that the thermal conductivity can be expressed as a sum of the two contributions, K_L due to longitudinal phonons and K_T due to transverse phonons, is valid for Mg_2Sn. The change of slope in the phonon conductivity versus temperature, which occurs at about 80°K, can be explained by the present approach of two-mode conduction (first proposed by Holland for Si and Ge, and later used by us for InSb, GaAs, and Si-Ge alloys[11]).

(2) It has been shown that almost all the heat transport at high temperatures is by transverse phonons.

(3) In order to account for the observed magnitude of phonon conductivity, especially near the maximum, one has to consider the resonant scattering of phonons by bound donor electrons. The elastic scattering part of the second-Born-perturbation results of Kwok's theory alone accounts for the observed values of the phonon conductivity near the maximum.

[11] C. M. Bhandari and G. S. Verma, Phys. Rev. **138**, A288 (1965); **140**, A2101 (1965).

ACKNOWLEDGMENTS

This work was supported by the University Grants Commission of India. The authors are grateful to Professor K. S. Singwi, Professor Vachaspati, Professor B. Dayal, and Dr. M. M. Joshi for their interest.

PHYSICAL REVIEW B VOLUME 1, NUMBER 2 15 JANUARY 1970

Nonrelativistic Energy-Band Structure of Au†*

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(Received 30 July 1969)

The composite wave variational method has been utilized to determine the electronic band structure, Fermi surface, and Fermi energy of Au in the nonrelativistic approximation. The crystal potential utilized in these calculations was constructed from Liberman, Waber, and Cromer's numerical Hartree-Fock solutions of the Dirac equation for the Au atom, including crystal exchange in the Slater $\rho^{1/3}$ approximation. Comparison is made with Shoenberg's experimental determination of Fermi-surface parameters using the de Haas–van Alphen effect.

I. INTRODUCTION

THE work reported here is an application of the composite wave variational method[1,2] (CWV) to calculation of the energy-band structure of gold. This marks the first application of this technique to an investigation of the band structure of a heavy element. The previous applications of this method have been to calculations of the band structure of the light alkalis,[1] x-ray scattering factors, and charge densities for Li,[3] and to positron annihilation in the alkalis.[4]

In Ref. 1 (SM), we presented several variational principles for the energy which apply to trial wave functions which are discontinuous on a surface within a unit cell in the crystal.[5] These expressions, which are at the heart of the CWV method, lead directly to the various forms for the matrix elements and secular equation given in SM. They also lead directly to the rapidly convergent iterative procedure for solving the secular equation which is a major advantage of the CWV method,[6] and which is discussed in detail in Sec. II 4 of SM.

In this calculation we make use of a crystal potential which was constructed by superposing Liberman, Waber, and Cromer's[7] numerical Hartree-Fock solutions of the Dirac equation for gold, including a crystal exchange contribution in the Slater $\rho^{1/3}$ approximation.[8] The energy bands have been plotted out in a number of symmetry directions and also $E(\mathbf{k})$ has been calculated at a large number of general points. This has enabled a precise determination of the Fermi surface. Comparison is made with Shoenberg's[9] experimental determination of Fermi-surface parameters using the de Haas–van Alphen effect.

† Supported in part by U. S. Army Research Office (Durham), under Contract No. DA-31-124-ARO-D-307.
* The bulk of this research was performed at the Polytechnic Institute of Brooklyn, Brooklyn, N. Y. 11201.
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[6] It should be pointed out that Loucks (Ref. 5) has not made optimal use of the variational principle for discontinuous wave functions in his relativistic calculations since he does not take advantage of the iterative procedure, described in Ref. 1, for solving the secular equation.
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