

Scattering of Phonons by Vacancies

C. A. Ratsifaritana¹ and P. G. Klemens²

Received July 1, 1987

The scattering of phonons by vacancies is estimated by a perturbation technique in terms of the missing mass and the missing linkages. An argument is given why distortion effects can be disregarded. The resonance frequency of the defect is sufficiently high so that resonance effects can be disregarded for phonons in the important frequency range for thermal conduction. The theory is applied to the thermal resistance by vacancies in cases where the vacancy concentration is known: potassium chloride with divalent cations, nonstoichiometric zirconium carbide, and tin telluride.

KEY WORDS: phonons; potassium chloride; thermal resistance; tin telluride; vacancies; zirconium carbide.

1. INTRODUCTION

Scattering of phonons by point defects in crystals was treated theoretically [1] using perturbation theory and has since been treated by self-consistent methods, using Green function techniques. These self-consistent methods are needed when the incident phonons are near or above an intrinsic resonance frequency of the defect. The physical consequences of those resonances have been reviewed by Maradudin [2]. At sufficiently low frequencies, however, one could expect perturbation theory to give good results provided the unperturbed Hamiltonian of the system is chosen so as to minimize the perturbation. When self-consistent calculations have been performed, there is, of course no need to revert to perturbation theory. However, most of these calculations have been confined to substitutional point defects, when the foreign atom differs only in mass from the parent

¹ Department of Physics, Ecole Normale III, University of Madagascar, Antananarivo, Malagasy Republic.

² Department of Physics and Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06268, U.S.A.

atom (isotopic defects) or differs in mass and nearest-neighbor force constants. Not all defects can be reduced to such simple terms.

Scattering of phonons by a vacancy has proved difficult to treat, since a vacancy is a strong local perturbation of the lattice and since it cannot be treated as a limiting case of a substitutional impurity. Yet vacancies occur frequently in sufficient concentration to affect the lattice thermal conductivity even at room temperature, so that it is important to have a theoretical estimate of their phonon scattering cross-section.

The object of this study is to treat the scattering of low-frequency phonons by vacancies. At low frequencies the vacancy can be regarded as a perturbation. It is argued that the perturbation is one that corresponds to the removal of the mass of one atom and the force constants of two atoms.

Even though perturbation theory is expected to hold only at low frequencies, calculations of thermal resistivity need not be confined to low temperatures. The low-frequency phonons make a surprisingly important contribution to the thermal conductivity even at ordinary and high temperatures, and the point-defect thermal resistivity is determined by the scattering cross section at such low frequencies as to allow the results of perturbation theory to be still applied [3].

In order to justify our simple method of estimating the perturbation, we must show that the distortion of the lattice around the vacancy is of little consequence to phonon scattering. Also, to justify perturbation theory one must show that the characteristic resonances of the vacancy lie high enough so as not to influence the scattering at the frequencies important to the thermal conductivity.

2. SCATTERING OF PHONONS BY VACANCIES

The phonon relaxation rate due to point defects is, at low frequencies, of the form

$$1/\tau = B\omega^4 \quad (1)$$

where ω is the angular frequency. The coefficient B depends on the nature of the point defect and is proportional to the concentration.

Following the notation of an earlier review [4], let the unperturbed Hamiltonian be

$$H^0 = \sum_{\mathbf{q}} M\omega^2 a^*(\mathbf{q}) a(\mathbf{q}) \quad (2)$$

where M is the average atomic mass, the summation is over all normal modes \mathbf{q} , and the displacement amplitudes $a(\mathbf{q})$ and $a^*(\mathbf{q})$ include phonon annihilation and creation operators, so that

$$a(\mathbf{q}) = (\hbar/M\omega)^{1/2} N^{1/2} \quad (3)$$

and $a^*(\mathbf{q})$ contains the factor $(N+1)^{1/2}$, where N is the initial number of phonons in the mode.

Writing the perturbation Hamiltonian due to defects in the form

$$H' = \sum_{\mathbf{q}, \mathbf{q}'} c(\mathbf{q}, \mathbf{q}') a^*(\mathbf{q}') a(\mathbf{q}) \quad (4)$$

the relaxation rate of a lattice mode \mathbf{q} can be shown to be

$$1/\tau = \sum_{\mathbf{q}'} |c(\mathbf{q}, \mathbf{q}')|^2 \frac{2}{M^2 \omega \omega'} \frac{1 - \cos(\omega - \omega') t}{t(\omega - \omega')^2} \quad (5)$$

Here the sum is over all normal modes \mathbf{q}' , i.e., over all wave vectors and polarizations. The time parameter t in the resonance factor disappears on summation. In Eq. (5) it was assumed that the perturbed region or scattering center is small compared to the wavelength and that $|c(\mathbf{q}, \mathbf{q}')|^2$ is just a function of ω , so that scattering is isotropic. Thus,

$$1/\tau = 2\pi(M^2\omega^2)^{-1} |c(\omega)|^2 g(\omega) \quad (6)$$

where $g(\omega)$ is the number of lattice modes in the frequency interval $d\omega$ about ω .

Choosing a Debye model for $g(\omega)$ with phonon velocity v

$$g(\omega) = 3(2\pi^2 v^3)^{-1} \omega^2$$

Consider now a single substitutional defect of mass difference ΔM in a crystal of G atoms, the perturbation is

$$H' = \frac{1}{2} \Delta M (\dot{u})^2 \quad (7)$$

where \dot{u} is the displacement velocity of the defect atom. Expressing u in terms of a superposition of waves, one finds

$$|c(\omega)|^2 = (1/12)(\Delta M/G)^2 \omega^4 \quad (8)$$

and one obtains

$$\frac{1}{\tau} = \frac{a^3}{G} \left(\frac{\Delta M}{M} \right)^2 \frac{\omega^4}{4\pi v^3} \quad (9)$$

where a^3 now denotes the atomic volume.

Let us now consider a vacancy on the basis of the same model. A vacancy is equivalent to removing from the material one atom and all the linkages between that atom and its neighbors. The missing mass of the

atom implies the removal of kinetic energy equal to the kinetic energy residing in that atom, i.e.,

$$T' = \frac{1}{2}M(\dot{u})^2 \quad (10)$$

where u is the displacement of the missing atom due to all the lattice waves. Similarly, the removal of a linkage between an atom (for convenience located at the origin) and a neighbor l implies the removal of potential energy

$$V' = \frac{1}{2} \sum_l k_l [u(l) - u(0)]^2 \quad (11)$$

where k_l is the (tensor) force constant of the linkage.

Now, according to the virial theorem, the potential and kinetic energies of the crystal are equal, and so are the time averages of T and V pertaining to one atom. However, since every linkage is shared by two atoms, V' is then twice the potential energy pertaining to one atom, or on the average $V' = 2T'$. Thus one may treat the energy as equivalent to an isotopic defect of strength $\Delta M = 3M$, and one may obtain for the relaxation rate

$$\frac{1}{\tau} = \frac{9a^3}{G} \frac{\omega^4}{4\pi v^3} \quad (12)$$

This simple result is the basis of our calculations. It is necessary, however, to justify it by showing that distortion of the lattice is unimportant and, also, that the vacancy does not have any low-lying mechanical resonances since resonances substantially increase scattering near the resonance frequency and above it, if the resonance frequency is well below the Debye frequency.

3. THE ROLE OF DISTORTION

It is important to examine the role of the strain field in scattering of phonons since strain would change the local value of ω for a fixed \mathbf{q} , thus contributing to the perturbation.

Consider the crystal as a continuous medium with a spherical inclusion of radius r_0 . The displacement field is given by the expression

$$\begin{aligned} \mathbf{D}(\mathbf{r}) &= A\mathbf{r}/r^3 + E\mathbf{r}, & r > r_0 \\ &= D\mathbf{r}/r, & r < r_0 \end{aligned} \quad (13)$$

where \mathbf{r} denotes the position relative to the center of the inclusion or scattering center.

The term $E\epsilon$ can be discarded because it expresses a uniform dilation and therefore does not contribute to the scattering of phonons.

It has been shown [1] that the perturbation Hamiltonian due to a displacement field $\mathbf{D}(\mathbf{r})$ is

$$H' = -\frac{2\eta M}{G} \sum_{\mathbf{r}, \mathbf{q}, \mathbf{q}'} \omega \omega' [\nabla \cdot \mathbf{D}(\mathbf{r})] e^{i(\mathbf{q} - \mathbf{q}') \cdot \mathbf{r}} a^*(\mathbf{q}') a(\mathbf{q}) \quad (14)$$

where η is the Grüneisen parameter. But $\nabla \cdot \mathbf{D}(\mathbf{r}) = 0$, and at first sight this model does not lead to any phonon scattering. Nevertheless, an analogy can be drawn between the strain field and the electromagnetic field caused by a point charge as was done by Carruthers [5]. Thus,

$$\mathbf{D}(\mathbf{r}) = (A/r^2) \delta(\mathbf{r} - \mathbf{x}) \quad (15)$$

where \mathbf{x} is the location of the scattering center.

The δ function implies that the contribution comes from the scattering center. In the case of the vacancy, it follows that distortion causes no additional disturbance since the linkages at this location have been removed and therefore cannot be modified by the distortion.

However, since the nearest linkages are shown to be so important, it is necessary to consider a discrete lattice. Let us first assume that the linkages are present and let us make an estimate of their contribution.

In the continuum treatment, the summation over \mathbf{r} in Eq. (14) is replaced by an integration, giving $4\pi A/a^3$, where A is related to the radius R of the vacancy and ΔR , the displacement of the atoms nearest to the vacant site, by

$$A = R^2 \Delta R \quad (16)$$

with ΔR negative for an inward displacement. We then obtain

$$c(\mathbf{q}, \mathbf{q}') = -(8\pi/Ga^3) \eta MR^2 \Delta R \omega' \omega \quad (17)$$

and replacing a^3 by $(4\pi/3) R^3$, we obtain

$$c(\mathbf{q}, \mathbf{q}') = -(6M/G) \eta (\Delta R/R) \omega' \omega \quad (18)$$

Let us now perform analogous calculations on a discrete model. The potential energy of one lattice site in the unperturbed crystal can then be written as

$$E_p = \lambda/2G \sum_{\mathbf{l}, \mathbf{q}, \mathbf{q}'} [\mathbf{l} \cdot \boldsymbol{\sigma}(\mathbf{q})][\mathbf{l} \cdot \boldsymbol{\sigma}(\mathbf{q}')] e^{i\mathbf{x} \cdot (\mathbf{q} - \mathbf{q}')} \times (1 - e^{i\mathbf{a}\mathbf{l} \cdot \mathbf{q}})(1 - e^{i\mathbf{a}\mathbf{l} \cdot \mathbf{q}'} a(\mathbf{q}) a^*(\mathbf{q}') \quad (19)$$

where \mathbf{I} is a unit vector giving the direction of the neighboring atoms, λ is the force constant for relative displacement in the direction of linkage. Also, $\boldsymbol{\sigma}(\mathbf{q})$ is the unit vector denoting the polarization of wave \mathbf{q} .

A force constant change $\delta\lambda$ will give rise to a velocity change δv related by

$$\delta\lambda = 2(M/a^2) v \delta v \quad (20)$$

A change in the velocity in turn causes a change in the potential and kinetic energies, so that the perturbation Hamiltonian becomes

$$H' = \frac{2M}{Ga^3} \sum_{\mathbf{I}} \sum_{\mathbf{q}, \mathbf{q}'} v \delta v(\mathbf{I}) [\mathbf{I} \cdot \boldsymbol{\sigma}(\mathbf{q})] [\mathbf{I} \cdot \boldsymbol{\sigma}(\mathbf{q}')] (1 - e^{ia\mathbf{I} \cdot \mathbf{q}}) (1 - e^{ia\mathbf{I} \cdot \mathbf{q}'}) a(\mathbf{q}) a^*(\mathbf{q}') \quad (21)$$

where the summation is over all the disturbed linkages denoted by \mathbf{I} . In the long wavelength limit we have $1 - e^{ia\mathbf{I} \cdot \mathbf{q}} \simeq -ia\mathbf{I} \cdot \mathbf{q}$ and we obtain

$$c(\mathbf{q}, \mathbf{q}') = \frac{2M}{G} \sum_{\mathbf{I}} v \delta v(\mathbf{I}) [\mathbf{I} \cdot \boldsymbol{\sigma}(\mathbf{q})] [\mathbf{I} \cdot \boldsymbol{\sigma}(\mathbf{q}')] (\mathbf{I} \cdot \mathbf{q}) (\mathbf{I} \cdot \mathbf{q}') \quad (22)$$

and δv is related to ΔR by the expression

$$\delta v/v = -\xi \Delta R/R \quad (23)$$

where ξ is an anharmonicity coefficient.

Treating all directions as uncorrelated

$$c(\mathbf{q}, \mathbf{q}') = -\frac{2M}{3G} \xi \sum_l \Delta L(l) R^{-1} \omega \omega' \quad (24)$$

where $\Delta L(l)$ specifies the change in length of a linkage $l = a\mathbf{I}$ and is a fraction of the displacement ΔR of the nearest neighbors.

Using a simple cubic lattice and assuming that the magnitude of the displacement field at a given lattice site falls off like the square of the distance from the vacancy center as in Eq. (13), we evaluate the summation over the disturbed linkages by considering successive shells around the vacancy center [6]. We obtain

$$c(\mathbf{q}, \mathbf{q}') = -3.73(M/G) \xi (\Delta R/R) \omega' \omega \quad (25)$$

If the six nearest linkages are considered to be present, $6\Delta R$ should be added to $\sum_l \Delta L$, so that

$$c(\mathbf{q}, \mathbf{q}') = -7.73(M/G) \xi (\Delta R/R) \omega' \omega \quad (26)$$

Only first-neighbor interactions are taken into account in these calculations; the consideration of the second nearest-neighbor interactions is expected to decrease these coefficients in absolute value.

We can compare Eq. (26) to its analogue in the continuum approximation, Eq. (18), for the case where the nearest linkages are included. The difference is less than 15% since ξ is normally smaller than the Grüneisen parameter.

Going back to Eq. (8), in which ΔM is replaced by $3M$, we get

$$|c(\omega)| = \left(\frac{3}{4}\right)^{1/2} M\omega^2/G \quad (27)$$

The contribution of the strain field, excluding the nearest linkages, becomes

$$|c(\omega)| = 3.73\xi(\Delta R/R) M\omega^2/G \quad (28)$$

Even if $\xi \Delta R/R$ were as large as 0.1, the distortion would make a contribution to $|c(\omega)|$ no more than about half of that given by Eq. (27). However, Eq. (28) is probably an overestimate, since all the linkages were made to contribute in the same sense. It thus appears that the distortion effects can be neglected for vacancies.

4. LOW-LYING RESONANCES

The perturbation method is valid provided that there are no low-lying resonances since resonances change the scattering appreciably if they are in the low portion of the frequency spectrum. Also, the exact form of the scattering at high frequencies is relatively unimportant to the thermal conductivity, so that the effect of any resonances at high frequencies is not important. Therefore, a detailed investigation of the dynamical properties of the solid containing a vacancy is essential to test that there are no resonances at low frequencies, before we apply the result of perturbation theory.

In general, the vibrational properties of a point defect are determined by the changes of neighboring force constants and the difference between its mass and that of the normal atom of the perfect crystal. Particular resonance frequencies ω_0 which are the solutions of the equations of motion are associated with the defect and the positions of ω_0 with respect to the bands of allowed phonon frequencies of the host crystal are critical for the phonon scattering problem. Two important cases arise.

(1) If ω_0 is higher than the frequencies which can propagate as lattice waves through the crystal, or if ω_0 is inside a gap between branches (for the case of non-Bravais lattices or polyatomic crystals), then non-

propagating or localized modes exist and their displacement field will fall off exponentially with the distance from the defect.

(2) If ω_0 is within the bands of allowed phonon frequencies of the crystal, we can have a situation referred to as a resonance state or pseudolocalized mode in which the defect oscillates almost independently of its surroundings. The most important effect is the strong scattering of phonons of frequencies close to ω_0 if the value of $\omega_0 < \frac{1}{2}\omega_D$. This in turn will give rise to a pronounced depression in the thermal conductivity curve.

The equations of motion of a simple cubic lattice containing one vacancy was set up in the notation of Elliott [7]. The vacancy was represented simply by removing the mass and the nearest longitudinal force constants. The equations of motion contain the eigenvalues and frequencies of the dynamical matrix of the perfect lattice, a longitudinal force constant λ between nearest neighbors, the mass M , and the frequency of vibration ω at which the lattice is being excited. The details, which follow the method of Dawber and Elliott [8], can be found in Ref. 6. The equations simplify if a Debye spectrum is assumed. The Debye frequency ω_D is related to λ and M by

$$\lambda/M = (6\pi)^{-2/3} \omega_D^2 \quad (29)$$

For modes of spherical symmetry the resonance frequency $\omega_0 = x\omega_D$ is the solution of

$$x \ln(1+x) - x \ln(1-x) = 2 + \left(\frac{2}{3}\right)(6\pi^2)^{2/3} \quad (30)$$

and for these modes $\omega_0 = 0.97\omega_D$.

For modes of lower symmetry the equations of motion are more complicated, and the resonance equation is the vanishing of a determinant. In this case it is not possible to find a closed equation for the resonance frequency, but it was possible to show by substitution that there is no resonance frequency below $\frac{1}{2}\omega_D$. Details can be found in Ref. 6.

Since there are no low-lying resonances, the results of perturbation theory can be used with confidence not only in the lower half of the frequency spectrum, but also at higher frequencies, since the effects of resonance are large only if ω_D/ω_0 is large.

It must be stated that we have taken a simple model using only nearest-neighbor forces and omitting force constants for transverse relative displacements. It is possible, but unlikely, that our conclusions would not be valid for a more general model, unless the defect lacked structural rigidity, as would be the case of two missing oxygen atoms in SiO_2 .

The present conclusion is apparently contradicted by the results of Schwartz and Walker [9], who observed an inflection in the thermal con-

ductivity of KCl at 30 K, induced by a variety of divalent impurities. They attributed this to resonance scattering by the vacancies accompanying these impurities. However, it was not known at that time that the top of one of the transverse branches lies at roughly four times that frequency, i.e., at the apparent resonance frequency [10]. Since the point-defect scattering of Eq. (1) contains a factor ω^2 which represents the density of states $g(\omega)$, a maximum in $g(\omega)$ would lead to enhanced scattering similar to resonance scattering. However, this enhanced scattering would be present for any point defect (or, for that matter, for any defect), no matter what its nature may be. Although these authors were probably correct in attributing the excess scattering at least in part to vacancies, the maximum in the scattering is not due to a mechanical resonance of the vacancy, but due to a maximum in $g(\omega)$ due to the accumulation of modes at a zone boundary. This, of course, was not known when Ref. 9 appeared.

5. APPLICATIONS

To test the theory, a comparison is made with thermal conductivity measurements on solids containing known vacancy concentrations: potassium chloride with divalent solutes, nonstoichiometric zirconium carbide, and tin telluride with tin vacancies.

5.1. Vacancies in Potassium Chloride

The substitution of a divalent cation in place of the potassium ion creates a vacancy in the potassium sublattice so as to preserve electric charge neutrality. It had been suggested [11] that this may be the source of the point-defect resistance which is apparent in the early measurements by de Haas and Biermasz [12]. To test this hypothesis, Slack [13] added CaCl_2 into KCl crystals and measured their thermal conductivity. He used a radioactive tracer technique to determine the calcium content. He concluded that there was a point-defect resistance even in the absence of calcium. He attributed this to isotopic mass-defect scattering of the phonons and was the first to recognize the importance of this mechanism. He was also able to measure the additional thermal resistance due to calcium and its accompanying vacancy. However, to deduce the strength of the corresponding point-defect scattering, one has to take account of "normal," i.e., momentum-conserving, three-phonon processes, and Slack used the only treatment available at that time [11], which treats the normal processes as very strong at low frequencies but neglects them at high frequencies. This inconsistency was removed by Callaway [14]. That treatment, published 2 years after Slack's paper, has since become standard

in analyzing thermal conductivity data. It thus seems worthwhile to reevaluate Slack's measurements using Callaway's treatment to deduce the strength of the point-defect measurement. It will be seen that this reevaluation does not change the deduced strength of point-defect scattering very much.

Slack [13] measured the thermal conductivity from 2 to 30 K of six KCl crystals: two were free of CaCl_2 and the others had concentrations of calcium ions ranging from 0.6 to 2×10^{-4} per cation. These should have an equal vacancy concentration, and the vacancies could be associated with the divalent impurities. It appears probable that the specimens of higher concentration also contain colloid inclusions; therefore the present analysis is restricted to a pure sample (Slack's sample A) and to sample N, containing 0.006% divalent cations, or 0.003% on a per-atom basis.

The point-defect relaxation rate is expressed in a form equivalent to Eq. (9):

$$1/\tau(\omega) = B\omega^4 = 3a^3(G\pi v^3)^{-1} S^2\omega^4 \quad (31)$$

where S^2 is a measure of the strength of point-defect scattering in the notation of Ref. 1.

Using Callaway's method [14], the pure sample was analyzed in terms of boundary scattering, point-defect scattering, and normal and Umklapp three-phonon processes. The best fit was obtained with the following relaxation rates.

Boundary scattering with a constant mean free path L :

$$1/\tau_B = v/L = 2.69 \times 10^5 \text{s}^{-1} \quad (32)$$

Point-defect scattering, expressed in the form of Eq. (31):

$$B_A = 2.24 \times 10^{-43} \text{s}^3 \quad (33)$$

The theoretical value of B for isotope scattering is $1.33 \times 10^{-43} \text{s}^3$, so that the observed value of B is almost twice that value.

Umklapp processes:

$$1/\tau_u = 1.5 \times 10^{10} x \exp(-100/T) \text{s}^{-1}, \quad (T \text{ in K}) \quad (34)$$

where x is the "reduced frequency" $h\omega/2\pi kT$.

Normal processes with the frequency and temperature dependence expected from the theory of Landau and Rumer [15]:

$$1/\tau_N = 30 \times T^5 \quad (35)$$

This value is lower than the theoretically expected one by roughly a factor 5.

With these parameters, Slack's thermal conductivity curve for his pure sample A could be fitted over the entire temperature range, with only a minor deviation (less than 5% above the measured curve) around 11 K [6].

Using the same parameters except for an increase in point-defect scattering for example N, the best fit was obtained with a value for B of

$$B_N = 8 \times 10^{-43} \text{s}^3 \quad (36)$$

The fit is not as good as for sample A. The theoretical curve departs from the observed one near the maximum at 6 K and lies progressively lower as the temperature is increased. A decrease in B_N raises the curve markedly at low temperatures and causes the curves to cross above 6 K, while an increase in B_N makes the theoretical curve fall below the observed one at all temperatures. The departure of the curves at best fit is in the same sense as would be caused by small clusters, since they would enhance the resistance at low temperatures relative to that at higher temperatures. The optimum fit gives greatest weight to the low temperatures where the conductivity is determined by boundary and point-defect scattering and is not very sensitive to three-phonon processes.

Subtracting Eq. (33) from Eq. (36) one obtains for the additional point defects

$$B = 5.8 \times 10^{-43} \text{s}^3 \quad (37)$$

Expressing B in terms of Eq. (31), using for $1/G$ the concentration of impurity cation per atom, i.e., 3×10^{-5} , one obtains for the calcium ion plus the vacancy

$$S^2 = 1.1 \quad (38)$$

This is not very different from the value of $S^2 = 1.4$ obtained by Slack, not surprisingly, since in both analyses the greatest weight was given to the temperature below the maximum. What the present analysis shows is that the thermal conductivity at higher temperatures demands less scattering at frequencies above about 5×10^{11} Hz or 3×10^{12} rad · s⁻¹ than given by Eq. (34). This is in the opposite sense to what one would expect from resonance scattering.

The present theory for scattering by the vacancy predicts

$$S = S_1 + S_2 \quad (39)$$

where

$$\begin{aligned} S_1 &= (12)^{-1/2} \Delta M/M = -0.30 \\ S_2 &= (12)^{-1/2} (-2) = -0.58 \end{aligned} \quad (40)$$

Here S_1 is due to the missing mass, except that $\Delta M/M$ is increased slightly in magnitude to 1.05 because K is slightly heavier than the average atomic mass of KCl; $S_2 = -2$ is due to the missing linkages. Thus $S = -0.88$, and for the isolated vacancy $S^2 = 0.77$.

For the Ca ion in place of K, $S_1 = 0.02$ and is thus negligible, while the term S_2 , describing the force constant perturbation, is not known. However, it is probable that S_2 is positive, and therefore S is positive. If the two point defects were associated, their contribution to S would be in opposition and their combined scattering parameter S^2 would be less than 0.77. If the vacancy and calcium ion are disassociated, both would contribute to S^2 additively, and the combined parameter S^2 would be larger than 0.77. Since the thermal conductivity is fitted with $S^2 = 1.1$, it seems probable that the two point defects are not associated. With a cation concentration of only 6×10^{-5} and a binding energy of 0.32 eV [13], it is probable that most defects are not associated. If this is accepted, the overall thermal resistance is not inconsistent with the calculated vacancy scattering cross section.

5.2. Carbon Vacancies in Zirconium Carbide

Taylor and Storms [16] measured the high-temperature thermal conductivity of nonstoichiometric ZrC with various concentrations of carbon vacancies. Around room temperature one can deduce the electronic component of the thermal conductivity from the electrical conductivity using the Sommerfeld value of the Lorenz ratio and thus deduce the lattice component, which is a substantial fraction of the total.

At and above the Debye temperature, the lattice thermal conductivity of a solid containing point defects can be expressed as [17]

$$\kappa(T) = \kappa_0(T)(\omega_0/\omega_D) \tan^{-1}(\omega_D/\omega_0) \quad (41)$$

where ω_0 is the frequency at which the intrinsic and the point-defect scattering are equal, ω_D is the Debye frequency, and $\kappa_0(T)$ is the thermal conductivity in the absence of point defects. The value of ω_0 depends on the intrinsic and the point-defect relaxation rate, and $\omega_0^2 \propto T/c$, where c is the defect concentration. The defect concentration (carbon vacancies per carbon atom) varied from 3.5 to 31.8%. The theoretical concentration dependence and Eq. (41) were used to find $\kappa_0(300) = 0.8 \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$,

while Taylor and Storms [16] suggested a value of about $0.5 \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$ from visual inspection of the concentration dependence.

With $\kappa_0(300)$ thus determined, one can obtain ω_0/ω_D for various concentrations. Writing the point-defect relaxation as $B\omega^4$ and expressing the intrinsic relaxation rate

$$\frac{1}{\tau_0} = b\omega^2 T \quad (42)$$

in terms of κ_0 through the relation $\kappa_0 = 3vk/(\omega_D^2 bT)$, and also using $\omega_0^2 = bT/B$ and $\omega_D/v = (6\pi^2 n)^{1/3}$, where n is the number of atoms per unit volume, one finds

$$B = (6\pi^2 n)^{1/3} k/[2\pi^2 \kappa_0(T) \omega_0^2] \quad (43)$$

Expressing B in terms of S^2 using Eq. (31), one obtains

$$B = 6.48 \times 10^{-41} S^2/G S^3 \quad (44)$$

where G is the number of atoms per vacancy. Comparing this with the values of ω_0 determined for various concentrations and using Eq. (43), a good fit was obtained for $S^2 = 0.98$.

The theory, modified for the fact that the missing mass is only 14/52 of the average mass, yields

$$S^2 = (12)^{-1} (2.27)^2 = 0.43 \quad (45)$$

so that the observed scattering cross section is roughly twice the theoretical one.

While the agreement between theory and experiment is not good, it should be noted that the experimental value of S^2 depends strongly on κ_0 and that a smaller value of κ_0 would have increased ω_0 and decreased B , thus reducing the discrepancy.

5.3. Tin Vacancies in Tin Telluride

Tin telluride also occurs in a nonstoichiometric form, and the concentration of tin vacancies can be determined from the carrier concentration. The thermal conductivity of several tin telluride samples was measured by Damon [18]. He separated the thermal conductivity into an electronic and a lattice component by using the Sommerfeld value of the Lorenz ratio at 100 K. Since the Debye temperature is 130 K, this is high enough to use Eq. (41) to describe the lattice thermal conductivity in the presence of point defects.

The value of κ_0 was again obtained by extrapolation and at 100 K $\kappa_0 = 0.13 \text{ W} \cdot \text{cm}^{-1} \cdot \text{K}^{-1}$. For a vacancy concentration of 2.5×10^{-3} per atom, one finds $\omega_0/\omega_D = 0.375$. From Eq. (43) one can find a value of B , and from Eq. (31) a corresponding value of S^2 . The value found in this way is $S^2 = 0.89$. The theoretical value, since the two atoms have nearly equal weight, is $S^2 = 0.75$. It is satisfactory that in this case, where both the vacancy concentration and κ_0 are determined with reasonable confidence, the agreement between theory and measurement is good.

ACKNOWLEDGMENT

This work was completed while one of us (C.A.R.) was in receipt of a fellowship from the Council for the International Exchange of Scholars under the Fulbright Program.

REFERENCES

1. P. G. Klemens, *Proc. Phys. Soc. (London)* **A68**:1113 (1955).
2. A. A. Maradudin, in *Solid State Physics*, F. Seitz and D. Turnbull, eds. (Academic Press, New York, 1966), Vol. 18, p. 273.
3. P. G. Klemens, in *Thermal Conductivity*, R. P. Tye, ed. (Academic Press, London, 1969), Vol. 1, p. 1.
4. P. G. Klemens, in *Solid State Physics*, F. Seitz and D. Turnbull, eds. (Academic Press, New York, 1958), Vol. 7, p. 1.
5. P. Carruthers, *Rev. Mod. Phys.* **33**:92 (1961).
6. C. A. Ratsifaritana, Doctoral dissertation (University of Connecticut, Storrs, 1979).
7. R. J. Elliott, in *Phonons in Perfect Lattices and in Lattices with Point Defects*, R. W. H. Stevenson, ed. (Oliver and Boyd, Edinburgh, 1966).
8. P. G. Dawber and R. J. Elliott, *Proc. Phys. Soc. (London)* **81**:453 (1963).
9. J. W. Schwartz and C. T. Walker, *Phys. Rev.* **155**:959 (1967).
10. H. Bilz and W. Kress, *Phonon Dispersion in Insulators* (Springer, Berlin, 1979).
11. P. G. Klemens, *Proc. Roy. Soc. (London)* **A208**:108 (1951).
12. W. J. de Haas and T. Biermasz, *Physica* **4**:752 (1937).
13. G. A. Slack, *Phys. Rev.* **105**:832 (1957).
14. J. Callaway, *Phys. Rev.* **113**:1046 (1959).
15. L. Landau and G. Rumer, *Phys. Z. Sowjetunion* **11**:18 (1937).
16. R. E. Taylor and E. K. Storms, in *Thermal Conductivity 14*, by P. G. Klemens and T. K. Chu, eds. (Plenum Press, New York, 1975).
17. P. G. Klemens, *Phys. Rev.* **119**:507 (1960).
18. D. H. Damon, *J. Appl. Phys.* **37**:3181 (1966).