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Role of Longitudinal and Transverse Phonons in the Thermal Conductivity of Alkali Halides

D. P. Singh and G. S. Verma

Physics Department, Banaras Hindu University, Varanasi-5, India

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In the present paper we have explained the temperature dependence of the thermal conductivity of KCl and NaCl by considering the separate contributions of longitudinal and transverse phonons. It is found that the transverse phonons make a major contribution towards thermal transport in these alkali halides.

INTRODUCTION

The low-temperature thermal conductivity of doped and undoped alkali halides has been studied extensively from both an experimental and a theoretical viewpoint by two different groups, one under Pohl at Cornell and the other under Klein at Illinois. The work of the Cornell group has been reviewed by Pohl in three different review articles.[1-3] The group at Illinois has also done a large amount of work[4-6] of which the most recent and important is the work of Rosenbaum *et al.*[7] Many other workers have also studied the thermal conductivity of doped and undoped alkali halides.[8-10] These workers have been successful in explaining the experimental results using the Callaway model[11] in which no distinction is made between longitudinal and transverse phonons. This distinction is, however, essential in view of the different dispersive natures and different relaxation times for the two types of phonons. Using both a variational method[12] and a relaxation-time approach,[13-15] it has been shown that in semiconductors most of the heat is probably carried by transverse phonons. Such a possibility also exists for alkali halides. Therefore, it is desirable to estimate the separate contributions of transverse and longitudinal phonons towards the phonon conductivity of alkali halides. This is possible either with the Holland model[16] or the Sharma, Dubey, and Verma (SDV) model[14,15] of phonon conductivity. In the variational method a provision to estimate the separate contributions due to longitudinal and transverse phonons exists in the technique given by Hamilton and Parrott.[12] However, the variational method is very difficult to apply owing to the complexity of the calculations involved. In the present paper we have used the Holland model to estimate the separate contributions of transverse and longitudinal phonons towards the phonon conductivity of alkali halides. As typical examples of alkali halides, we have considered KCl and NaCl.

THEORY

In the Holland model the lattice thermal conductivity K is given by

$$K = K_L + K_{T_1} + K_{T_2}.$$

The subscripts T and L indicate transverse and longitudinal phonons.

In alkali halides the longitudinal phonon spectrum

is not a straight line; therefore, it is also neces-
sary to divide K_L into two parts, i.e.,

$$K_L = K_{L_1} + L_{L_2} .$$

The procedure for writing these conductivity in-
tegrals is discussed in several papers.[13,14,16]

The expressions for relaxation times due to dif-
ferent scattering processes have been studied ex-
tensively and are given below:

$$\tau_B^{-1} = v_s/LF, \qquad L = 1.12\, S^{1/2} \quad \text{(Casimir Ref. 17)},$$

$$\tau_i^{-1} = A\omega^4, \qquad A = \frac{V_0}{4\pi v_s^3} \sum_i f_i \left(1 - \frac{M_i}{\bar{M}}\right)^2$$

(Klemens, Ref. 18),

$$\tau_{L_1}^{-1} = B_{L_1}\omega^2 T^3, \qquad \tau_{T_1}^{-1} = B_{T_1}\omega T^4 \quad \text{(Herring, Ref. 19)},$$

low temperature,

$$\tau_{L_2}^{-1} = B_{L_2}\omega^2 T, \qquad \tau_{T_2}^{-1} = B_{T_2}\omega T \quad \text{(Klemens, Ref. 20)}$$

high temperature. Here v_s is the average phonon
velocity, S is the area of the rectangular cross
section of the crystal, V_0 is the molecular volume,
f_i is the fractional defect concentration of the ith
species of molecules, M_i is the mass of the ith
species of molecules, and $\bar{M}$ is the average molec-
ular mass. $B_{L_1}, B_{T_1}, B_{L_2},$ and B_{T_2} are adjustable
parameters and can be obtained from the best a-
agreement between the theoretical and experimental
values of thermal conductivity of a pure crystal
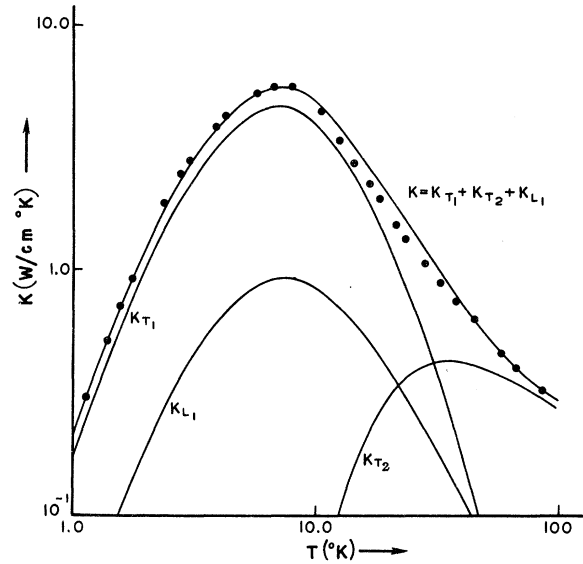over the entire temperature range. It should be noted

FIG. 1. Comparison of the theoretical values of pho-
non conductivity of pure KCl with experimental values.
Solid lines show the theoretical curves while the circles
denote the experimental points.

that the relaxation times due to three-phonon proces-
ses are not exact. They are simply the low-tempera-
ture (Herring) and high-temperature (Klemens) ap-
proximations of the exact relaxation times. Since K_{T_1}
and K_{L_1} give larger contribution to the total ther-
mal conductivity at low temperatures, we can use
the low-temperature approximation for $\tau_{T_1}^{-1}$ and
$\tau_{L_1}^{-1}$. Similarly, K_{T_2} and K_{L_2} give larger contribu-
tions at high temperature so we can use high-
temperature approximations for $\tau_{T_2}^{-1}$ and $\tau_{L_2}^{-1}$.

The other things required in the analysis of pho-
non conductivity by the Holland model are the phonon
velocities and the limits for the different conduc-
tivity integrals. These quantities can be calculated
from the experimental dispersion curves in the
appropriate direction.

Application to KCl and NaCl

The parameters used in the analysis are listed
in Table I. Velocities are obtained from the slopes
of the dispersion curves in the required frequency
range in the (100) direction which is the direction
in which the conductivity was measured. For KCl
we have used the dispersion curve measured by
Copley, Macpherson, and Timusk,[21] while for
NaCl we have used the dispersion curve measured
by Raunio and Rolandson.[22] Since the contribution
of K_{L_2} is very small as compared to other contri-
butions, we have neglected it in the present analy-
sis.

Figure 1 shows the results of the present analy-
sis of thermal conductivity of KCl. The contribu-

TABLE I. Parameters used in the analysis.

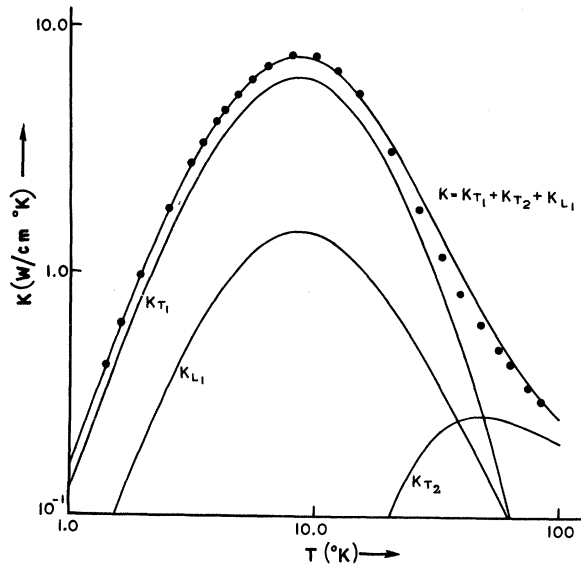|	KCl	NaCl
v_{T_1}	1.66×10^5 cm/sec	2.06×10^5 cm/sec
v_{T_2}	5.53×10^4 cm/sec	8.94×10^4 cm/sec
v_{L_1}	4.14×10^5 cm/sec	4.10×10^5 cm/sec
v_{L_2}	-1.13×10^5 cm/sec	-1.49×10^5 cm/sec
v_s	3.1×10^5 cm/sec	3.8×10^5 cm/sec
Θ_1	63 °K	88 °K
Θ_2	84 °K	126 °K
Θ_3	155 °K	206 °K
Θ_4	190 °K	244 °K
τ_B^{-1} (theory)	6.9×10^5 sec^{-1}	8.4×10^5 sec^{-1}
τ_B^{-1} (expt)	8.7×10^5 sec^{-1}	9.8×10^5 sec^{-1}
A (theory)	3.0×10^{-44} sec^3	3.0×10^{-44} sec^3
A (expt)	15.0×10^{-44} sec^3	7.0×10^{-44} sec^{-3}
B_{T_1}	1.8×10^{-10} deg^{-4}	8.1×10^{-11} deg^{-4}
B_{T_2}	6.3×10^{-6} deg^{-1}	1.5×10^{-5} deg^{-1}
B_{L_1}	9.0×10^{-22} sec deg^{-3}	4.3×10^{-22} sec deg^{-3}

FIG. 2. Comparison of the theoretical values of phonon conductivity of pure NaCl with experimental values. Solid lines show the theoretical curves while the circles denote the experimental points.

tion of each integral is shown separately. The experimental data are taken from Walker and Pohl.[23] The values of the various parameters are adjusted in the usual way. τ_B^{-1} and A are also treated as adjustable parameters. For comparison we have included their theoretical values in Table I. In Fig. 2 we show the results of the present analysis of NaCl. The experimental data are taken from Worlock.[24]

From Figs. 1 and 2 it is obvious that the agreement is excellent over a very large temperature range. For both materials the poorest fit occurs in the region in which K_{T_2} has its maximum, as might be expected since the values are highly sensitive to ω_1 which is one of the least accurately

determined parameters. Moreover, in this region the temperature dependences of the three-phonon relaxation times are also not correct.

On comparing our theoretical results with those of the previous workers,[6,7,23] we find that at low temperatures, particularly near the conductivity maximum, our results are much better than their results, but at higher temperatures ($T > 10$ °K) their results are better than our results. Since, in general, the effect of doping is to reduce the conductivity at low temperatures, our method will be more useful in the analysis of the thermal conductivity of the doped alkali halides.

It should be noted that $K_T = K_{T_1} + K_{T_2}$ and $K_L = K_{L_1}$ (K_{L_2} being negligible), so one can see from Figs. 1 and 2 that $K_T > K_L$ for both materials in the entire temperature range. Therefore, we can say that the transverse phonons are the major carriers of heat in alkali halides in the entire temperature range.

From Table I it is seen that for both materials the theoretical values of τ_B^{-1} are smaller than their adjusted values. This suggests that even in pure crystals of these alkali halides there are some other scattering mechanisms due to dislocations or grain boundaries. The theoretical values of A are also smaller in comparison with their adjusted values. These large adjusted values are perhaps due to other background impurities in the pure crystals that contribute to the Rayleigh scattering.

CONCLUSION

The most important feature of the present work is that it uses the known phonon spectrum in order to divide the heat flow into the contributions of longitudinal and transverse phonons. The present analysis shows that the Holland model can be successfully applied to explain the thermal conductivity of alkali halides. It is also found that the transverse phonons give a major contribution towards the thermal conductivity of alkali halides.

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Convergence of Reciprocal-Lattice Expansions and Self-Consistent Energy Bands of NaF†

N. E. Brener

Department of Physics and Astronomy, Louisiana State University, Baton Rouge, Louisiana 70803

and

J. L. Fry

Department of Physics, University of Texas, Arlington, Texas 76010

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A convergence study is made of the reciprocal-lattice expansion of linear-combination-of-atomic-orbitals integrals in NaF. Converged integrals are obtained by direct summation and by extrapolation after different numbers of terms. It is found that extrapolation procedures give simple accurate results and substantially reduce labor involved. Comparison is made with other methods for obtaining convergence. Converged integrals are used as a basis for a self-consistent Hartree−Fock−Slater energy-band calculation for NaF using methods previously developed. Some transition energies are presented and correlated with available optical data. Self-consistent charge densities in NaF differ only slightly from a linear combination of ionic charge densities, confirming the ionic nature of NaF.

I. INTRODUCTION

The linear-combination-of-atomic-orbitals (LCAO) method which was first proposed[1] in 1928 has only recently been developed to its full power.[2-11] While there are still some theoretical questions of its applicability to quantitative solid-state calculations, practical experience indicates that it not only is as accurate as other methods when done correctly, but also has great advantage in self-consistent calculations[5] or problems involving Brillouin-zone sampling or computation of matrix elements using Bloch wave functions. However, when reading the literature of LCAO or tight-binding calculations one must be careful to distinguish between approximate LCAO calculations and ones which are performed with new techniques. Neglect or approximation of multicenter integrals and inclusion of only limited numbers of neighbors usually means that the energy bands are qualitative at best. Discussions of the problems encountered in accurate LCAO procedures are given in Refs. 6, 11, and 12.

In this paper special attention is paid to convergence properties of the reciprocal-lattice series expansion of LCAO integrals. Some of the methods

used to facilitate summation of these series are discussed in Sec. II. In Sec. III, well-converged integrals for NaF are used to perform a self-consistent Hartree−Fock−Slater energy-band calculation.

II. CONVERGENCE OF LCAO INTEGRALS

The LCAO method employed here has been discussed elsewhere[2,3,7] and will not be presented again. Accuracy in LCAO energy bands requires a critical analysis of all approximations made. In this section attention is focused upon convergence of reciprocal-lattice expansions of various LCAO integrals.

Reciprocal-lattice sums are a result of expressing the crystal potential as a Fourier series in order to circumvent calculation of three-center integrals. Approximation or complete neglect of the difficult three-center integrals and failure to sum enough direct-lattice neighbors invalidated early efforts to use the LCAO method in first-principles calculations. The Fourier-series technique permits accurate evaluation of LCAO integrals and produces accurate energy bands.

Introduction of Gaussian orbitals instead of Slater (exponential) orbitals greatly simplifies and