# THERMAL CONDUCTIVITY OF Ne AND He$^4$ QUANTUM CRYSTALS

D. B. Benin†
Department of Physics and Astronomy, University of Rochester, Rochester, New York
(Received 20 March 1968)

Calculations of lattice thermal conductivities have been performed, using the self-consistent phonon approximation to treat the zero-point motion.

An important and challenging discrepancy exists between calculated and experimental lattice thermal conductivities of the lighter rare-gas solids. Julian[1] has performed calculations based on the Peierls theory[2-5] of Umklapp scattering of three harmonic-approximation phonons by an anharmonic interatomic potential. For Ar and Kr this calculation is in reasonable agreement with experiment, but is low by a factor of about 2 for Ne, despite the fact that the theory includes no thermal resistance due to defects or surfaces. Since in a light crystal the zero-point vibration about a lattice site may spread a particle over regions of considerable anharmonicity of the interatomic potential, the origin of the discrepancy may lie in use of the ordinary quantized theory of small oscillations to define harmonic phonons. The present calculation of the thermal conductivity of Ne is based on the self-consistent harmonic approximation,[6] and shows significantly improved agreement with experiment. A first calculation of the conductivity of an fcc model of He$^4$ is also reported.

In a strongly anharmonic crystal, for temperatures less than $\Theta_D$ the major correction to the Peierls theory of thermal conductivity arises from anharmonic contributions to the local equilibrium distribution.[3-5] This effect is a lattice-dynamical rather than transport-theoretical correction; that is, anharmonicity simply renormalizes the frequencies and lifetimes of the phonons involved in a Boltzmann equation for the transport process. In the self-consistent theory, a frequency renormalization results from variational choice of an effective harmonic Hamiltonian, whose force constants $H_{\vec{O}\vec{R}}^{\alpha\beta}$ coupling displacements in the $\alpha$ and $\beta$ directions from lattice sites of separation $\vec{R}$ are spatial averages of the derivatives of an assumed pair potential $\varphi(r)$, weighted with the normalized distribution function of the pair:

$$H_{\vec{O}\vec{R}}^{\alpha\beta}=-\int d\vec{r}\, g_R(\vec{r}-\vec{R})\frac{\partial^2\varphi(r)}{\partial r^\alpha\partial r^\beta}.$$

To this Hamiltonian we add an effective cubic anharmonic term by calculating the matrix element for scattering of three self-consistent phonons by the full anharmonic lattice potential. For pairwise central forces, the nonvanishing cubic anharmonic force constants obtained in this way also involve averaging of potential derivatives:

$$\begin{aligned}A_{\vec{O}\vec{R}\vec{R}}^{\alpha\beta\gamma}&=-A_{\vec{R}\vec{R}\vec{O}}^{\alpha\beta\gamma}\\&=-\int d\vec{r}\, g_R(\vec{r}-\vec{R})\frac{\partial^3\varphi(r)}{\partial r^\alpha\partial r^\beta\partial r^\gamma}\\&=-R^\alpha R^\beta R^\gamma R^{-3}A_1(|\vec{R}|)-[R^\alpha\delta^{\beta\gamma}+R^\beta\delta^{\gamma\alpha}+R^\gamma\delta^{\alpha\beta}]R^{-1}A_2(|\vec{R}|).\end{aligned}$$

A phonon Boltzmann equation is then written, with cubic terms treated in the Born approximation for the collision term (cf. Leibfried, Ref. 2). Thus further frequency shifts and ladder-diagram multiple scatterings are not included. A lower bound for the thermal conductivity $K$ of such a model is

$$K\left(\frac{T}{\Theta}\right)=\frac{256\sqrt{2}k}{5\pi^3\hbar}\left\{\frac{(\frac{1}{4}M\mu_2)^3}{(A_1+3A_2)^2l}\right\}\left\{\frac{(\Theta/T)^2\Omega^2}{C_1+C_2\Lambda+C_3\Lambda^2}\right\}. \quad (1)$$

Here $k$ is Boltzmann's constant, $l$ the nearest-neighbor spacing, $M$ the atomic mass, $\mu_2$ the second moment of the harmonic frequency spectrum,[7] and $\Theta$ the characteristic temperature[7] $\Theta_\infty{}^C$. Only nearest-neighbor force constants $A_1$ and $A_2$ have been retained, $\Lambda=A_2/(A_1+3A_2)$, and $\Omega(T/\Theta)$ and $C_i(T/\Theta)$ are dimensionless sums over dispersion curves. Equation (1) is a generalization of the expression derived by Julian,[1] whose model ignores zero-point motion entirely.

Within the framework of the ordinary quasiharmonic approximation, inclusion of zero-point effects in a Ne model results in a thermal conductivity much <u>smaller</u> than that found by Julian, since the predominant consequence of the lattice expansion due to zero-point pressure is a lowering of the energy a phonon contributes to the heat current. Thus it appears essential to account for anharmonicity in the elementary excitations themselves.

An iterative procedure (cf. Koehler, Ref. 6) has been performed to determine self-consistent force constants for a model Ne crystal of 1000 particles, interacting through a Lennard-Jones (6, 12) potential with parameters $\epsilon = 51.0\times10^{-16}$ erg, $\sigma = 2.77$ Å. The thermal conductivity of this model, calculated from Eq. (1), is shown in Fig. 1.

For solid helium, the short-range correlation in the motions of particles due to the repulsive core of $\varphi(r)$ must be taken into account explicitly.[8,9] Our procedure is to apply the self-consistent theory to a helium lattice with an effective interatomic potential

$$W = \tfrac{1}{2}\sum_{i\neq j}\langle f^2(r_{ij})\rangle^{-1} f^2(r_{ij}) \times[\varphi(r_{ij}) - \hbar^2(2M)^{-1}\nabla_{ij}^{\,2}\ln f(r_{ij})].$$

Here $\varphi(r)$ is the (6, 12) potential with parameters[9] $\epsilon = 14.11\times10^{-16}$ erg, $\sigma = 2.556$ Å, the expectation value is taken in the self-consistent harmonic ground state, and $f(r)$ is Nosanow's[9] short-range correlation function for He$^4$:

$$f(r) = \exp\{-0.1778[(\sigma/r)^{12} - (\sigma/r)^6]\}. \qquad (2)$$

Such a theory results from variation of the ground-state energy with respect to each force constant, after truncating Nosanow's cluster expansion at the pair term, and neglecting a correction of about 2% to the force constants which involves averages of $d^2f/dr^2$.

Calculations similar to those for Ne have been performed for an fcc model of solid He$^4$ at a volume 19.5 cc/mole. The ground-state energy of this model is $-4.69$ cal/mole; the thermal conductivity is shown in Fig. 2. The gross overestimate of the conductivity results because $f(r)$ of (2) falls too rapidly to zero inside the repulsive core of $\varphi(r)$. While this deficiency does not strongly affect the ground-state energy,[9] it becomes increasingly important in averages of higher derivatives of $W$, and leads to serious underestimation of the amount of anharmonic scattering from the repulsive core. It may be that the hard-core renormalization in solid He is not adequately simulated by as simple a pseudopotential as $W$, whose use can only be justified for a restricted class of short-range correlation func-

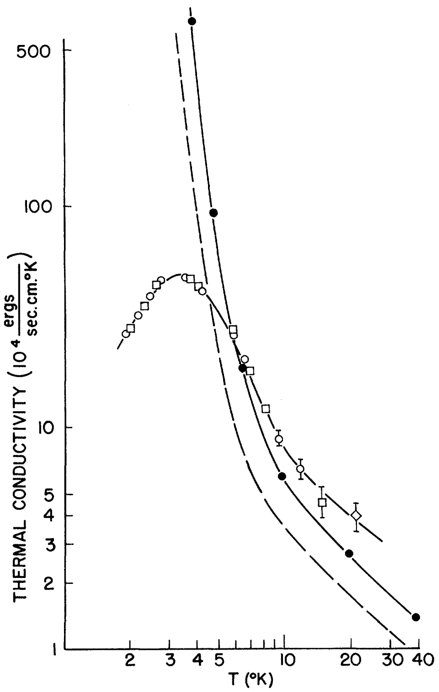

FIG. 1. Thermal conductivity of Ne. Experiment: G. K. White and S. B. Woods, Phil. Mag. <u>3</u>, 787 (1958). Dashed line: Julian's calculation (Ref. 1), with corrected lattice constant. Solid line: this work. Comparison between experiment and these calcluations is meaningful only to the right of the experimental maximum.

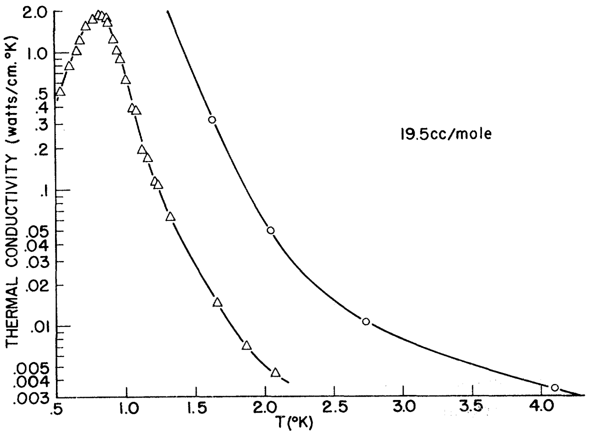

FIG. 2. Thermal conductivity of He$^4$. Experiment: B. Bertman, H. Fairbank, C. White, and M. Crooks, Phys. Rev. <u>142</u>, 74 (1966). Solid line: this work.

tions with the general features of (2).[10] In addition, a generalized treatment of phonon collisions, going beyond the Born approximation in the Boltzmann equation, may also be necessary (cf. Ref. 4).

The improvement of the Ne result presented here over those of the harmonic and quasiharmonic approximations indicates the value of extending the self-consistent approach to encompass phonon lifetime effects. Further study of such effects, and their full incorporation into the renormalization formalism, seem desirable. New, constant-volume measurements of the Ne conductivity should now be able to provide a more stringent test of any anharmonic theory, by producing a higher maximum at lower temperature than that shown in Fig. 1.

---

*Work supported by Grant No. 611-67 from the U. S. Air Force Office of Scientific Research. A preliminary report of this work was presented by D. B. Benin and R. S. Knox, Bull. Am. Phys. Soc. 12, 355 (1967).

Based on a thesis submitted in partial fulfillment of the requirements for the Ph. D. degree, University of Rochester.

†Present address: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, N. Y.

[1] C. L. Julian, Phys. Rev. 137, A128 (1965).

[2] R. E. Peierls, Ann. Physik 3, 1055 (1929). See also G. Leibfried, *Handbuch der Physik*, edited by S. Flügge, (Springer-Verlag, Berlin, Germany, 1955), Vol. 7, Part 1, p. 104; P. Carruthers, Rev. Mod. Phys. 33, 92 (1961); R. J. Jardy and W. C. Schieve, J. Math Phys. 7, 1439 (1966).

[3] J. Ranninger, Phys, Rev. 140, A2031 (1965).

[4] J. Ranninger, Ann. Phys. (N. Y.) 45, 452 (1967).

[5] K. Ishikawa, Phys. Status Solidi 21, 137 (1967).

[6] T. R. Koehler, Phys. Rev Letters 17, 89 (1966), and Phys, Rev. 165, 942 (1968); P. Choquard, quoted by Ranninger, Ref. 3; H. Horner, Z. Physik 205, 72 (1967).

[7] C. Domb and L. Salter, Phil. Mag. 43, 1083 (1952).

[8] T. R. Koehler, Phys, Rev. Letters 18, 654 (1967).

[9] L. H. Nosanow, Phys. Rev. 146, 120 (1966).

[10] J.-P. Hansen and D. Levesque, Phys. Rev. 165, 293 (1968); W. E. Massey and C.-W. Woo, Phys. Rev. 169, 241 (1968); G. Meissner, to be published.

---

# AUGER-LIKE RESONANT INTERFERENCE IN RAMAN SCATTERING FROM ONE- AND TWO-PHONON STATES OF $BaTiO_3$

D. L. Rousseau and S. P. S. Porto
Departments of Physics and Electrical Engineering,
University of Southern California, Los Angeles, California 90007

(Received 8 April 1968)

Resonant interference between one- and two-phonon states has been observed in $BaTiO_3$, and has been shown to obey the quantum mechanical formalism developed by Fano for Auger processes. By selecting different components of the differential polarizability tensor and by changing the propagation direction, the degree of interference could be varied over a wide range. The linewidth and line-profile parameters were determined for several different crystal orientations.

When a discrete energy state is superimposed on a broad continuum, the well-known phenomenon of resonant interference (Auger processes) may occur. In general, Auger interactions are characterized by (1) decomposition of the excited species through electron ejection or molecular fragmentation; (2) broadening and distortion of the absorption, emission, and scattering line shapes; and (3) weakening of emission lines to lower states from the discrete state. The wide range of electronic-state Auger resonances observed by electron scattering and ultraviolet absorption has been discussed by Burke[1] and Herzberg,[2] and the quantum mechanical formalism describing Auger transitions has been thoroughly developed by Fano and Cooper.[3,4] In this Letter we wish to report the Raman-scattering observation of a resonant interference between one- and two-phonon states of $BaTiO_3$ and to show that this interference may be completely described by the Fano formalism for Auger processes. The particular importance offered by Raman-spectroscopic observation of such processes is the ability to select a diversity of phonon propagation directions and differential polarizability tensors, and thereby drastically vary the degree of interference.

Recently there have been several Raman-scattering investigations of ferroelectric solids.[5-7] Since these materials have very large dielectric constants they exhibit very strong multiple-phonon scattering. For example, the Raman spec-