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Thermal conductivity of solid neon: An iterative analysis

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In this paper, the thermal conductivity of neon is obtained by means of a recently proposed iterative solution of the phonon Boltzmann equation. The potential used for the calculation is an effective Lennard-Jones potential to include quantum effects. Good agreement with the experimental data is obtained. [S0163-1829(97)07337-2]

I. INTRODUCTION

Rare-gas crystals are probably the simplest dielectric solids in which it is possible to study the phonon heat transport and the role of impurities, dislocations, and other scattering mechanisms and to compare the theoretical analysis with the experimental results[1–6] of several laboratories.

Previous analyses with a variational[7] and with an iterative solution technique[8,9] of the phonon Boltzmann equation[10,11] applied to argon and krypton gave a good agreement between the calculation and the experimental data.

The iterative technique[9] solves the Boltzmann equation without introducing adjustable parameters or relaxation time approximations[12] and does not need any special statement in the lattice model or in the adopted form of the trial function as in the variational approaches.[7,10,11,13,14] An ''*ab initio*'' numerical calculation from the interatomic forces of the lattice thermal conductivity is then possible: the only requirement is that the iteration procedure must be convergent.

In this framework, the choice of the potential and of the potential parameters plays a decisive role in the calculation and the comparison of the obtained thermal conductivity with the experimental data becomes a useful tool to discriminate between potentials.

For rare-gas solids, the usual choice is a Lennard-Jones potential that, as already told, in the case of argon and krypton gives good results. But in the case of neon, due to the lighter mass, the problem of taking into account the quantum effects due to the zero-point motion on the thermal resistivity is unavoidable:[1,6] it was previously analyzed by a phenomenological approach[15] and by a solution in the Ziman limit[5,10] of the heat-transport equation giving only qualitative agreement with the experimental data.

The problem of determining the thermal conductivity of neon is then worthy to be considered by means of a nonapproximate analysis in order to obtain a quantitative answer and a possible estimate of the role of quantum effects.

In this paper, we present the results obtained by means of the iterative tecnique using an effective Lennard-Jones potential[16] with parameters depending on the temperature: good agreement with the experimental data of Weston and Daniels[5] is obtained. Moreover, a comparison with the thermal conductivity obtained with the bare Lennard-Jones potential is made, confirming the essential role played by the effective potential.

II. THE MODEL AND THE ITERATIVE TECHNIQUE

The interatomic potential used in the present calculation is an effective Lennard-Jones[16]

$$V(r)=\Phi\left[\left(\frac{r_0}{r}\right)^{12}-\left(\frac{r_0}{r}\right)^{6}\right], \tag{1}$$

in which we replace $\Phi\rightarrow\Phi^*$ and $r_o\rightarrow r_o^*$, given by the following expressions:

$$\Phi^*=\Phi\{1-14.3x^{-1}+104.9x^{-2}\}, \tag{2}$$

$$r_o^*=r_o\{1+3.77x^{-1}\}, \tag{3}$$

where $x=3mk_BTr_o^2/\hbar^2$. Like in Ref. 16, let us assume that the major effect of the quantum correction is to produce an effective potential of the same form as the bare potential with parameters depending on the temperature. In spite of the lack of mathematical rigor, the use of this potential gives a quantitative agreement with the experimental results for the thermodynamical properties of neon.

The data used for the calculation are that of Ref. 16: $\Phi/k_B=146.8$ K, $r_o=2.79$ Å, where k_B is the Boltzmann constant.

From now on, let us disregard the asterisk, understanding by Φ Eq. (2). To describe the lattice model and the iterative technique, let us use the same notation of Ref. 9 from now on referred to as I.

Introducing the dimensionless parameter for the central potential $V(h)$:

$$\sigma_h=h_1^2\Phi^{-1}\left\{\frac{1}{h}\frac{\partial V(h)}{\partial h}\right\};\quad \rho_h=h_1^4\Phi^{-1}\frac{1}{h}\frac{\partial}{\partial h}\left\{\frac{1}{h}\frac{\partial V(h)}{\partial h}\right\} \tag{4}$$

with h the lattice site distance and h_1 the nearest-neighbor distance, we can write the equation for the frequency and polarization of a phonon with wave vector $\mathbf{q}$:

$$\sum_{\mathbf{h}}(1-\cos\mathbf{q}\cdot\mathbf{h})\left[\sigma_h\mathbf{e}+\frac{\rho_h}{h_1^2}(\mathbf{h}\cdot\mathbf{e})\mathbf{h}\right]=\frac{h_1^2m\omega^2}{\Phi}\mathbf{e}, \tag{5}$$

where the sum is running over all the fcc lattice sites, the position of each site being identified by the vector $\mathbf{h}$. The

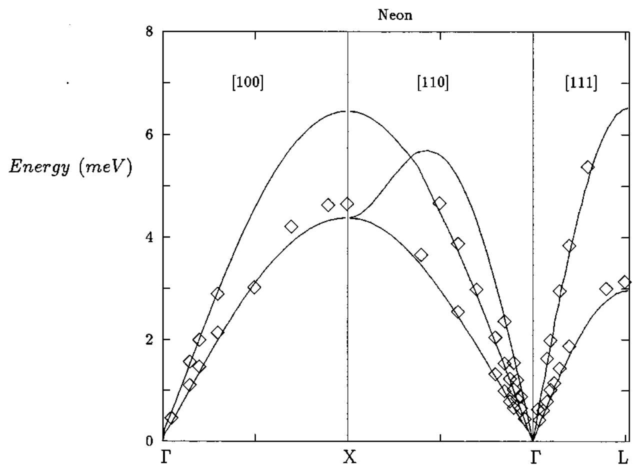

FIG. 1. Theoretical phonon-dispersion curves (continuous lines) for neon, in comparison with experimental data (Ref. 17).

dispersion relations obtained by means of Eq. (5) are in good agreement with the experimental data of Endoh, Shirane, and Skalyo[17] (see Fig. 1).

Calling n^o_{qp} the unperturbed distribution of phonons with wave vector $\mathbf{q}$ and polarization p and $\Psi_{\mathbf{q}p}$ the deviation function from this distribution, linked by the following relation:

$$n_{\mathbf{q}p}=n^o_{qp}-\Psi_{\mathbf{q}p}\frac{\partial n^o_{qp}}{\partial(\hbar\omega_{\mathbf{q}p})}\tag{6}$$

to the perturbed distribution $n_{\mathbf{q}p}$, we can write the linearized Boltzmann equation:

$$\begin{aligned}k_BT\mathbf{v}_{\mathbf{q}p}\cdot\nabla T\frac{\partial n^o_{qp}}{\partial T}={}&\sum_{\mathbf{q}'p',\mathbf{q}''p''}Q^{\mathbf{q}''p''}_{\mathbf{q}p,\mathbf{q}'p'}[\Psi_{\mathbf{q}''p''}-\Psi_{\mathbf{q}'p'}-\Psi_{\mathbf{q}p}]\\&+\frac{1}{2}\sum_{\mathbf{q}'p',\mathbf{q}''p''}Q^{\mathbf{q}'p',\mathbf{q}''p''}_{\mathbf{q}p}\\&\times[\Psi_{\mathbf{q}''p''}+\Psi_{\mathbf{q}'p'}-\Psi_{\mathbf{q}p}],\end{aligned}\tag{7}$$

$\mathbf{v}_{\mathbf{q}p}$ is the phonon group velocity. The sum is over all the three-phonon scattering processes, normal and umklapp. $Q^{\mathbf{q}''p''}_{\mathbf{q}p,\mathbf{q}'p'}$ and $Q^{\mathbf{q}'p',\mathbf{q}''p''}_{\mathbf{q}p}$ represent the probability rates of the three phonon processes $(\mathbf{q}p)+(\mathbf{q}'p')\rightarrow(\mathbf{q}''p'')$ and $(\mathbf{q}p)\rightarrow(\mathbf{q}'p')+(\mathbf{q}''p'')$, respectively,

$$\begin{aligned}Q^{\mathbf{q}''p''}_{\mathbf{q}p,\mathbf{q}'p'}={}&\frac{\pi\hbar}{16m^3N}\frac{n^o_{qp}n^o_{q'p'}(1+n^o_{q''p''})}{\omega_{\mathbf{q}p}\omega_{\mathbf{q}'p'}\omega_{\mathbf{q}''p''}}\\&\times\delta(\omega_{\mathbf{q}p}+\omega_{\mathbf{q}'p'}-\omega_{\mathbf{q}''p''})\mathcal{R}^+_{\mathbf{q}p,\mathbf{q}'p',\mathbf{q}''p''},\end{aligned}\tag{8}$$

$$\begin{aligned}Q^{\mathbf{q}'p'\mathbf{q}''p''}_{\mathbf{q}p}={}&\frac{\pi\hbar}{16m^3N}\frac{n^o_{qp}(1+n^o_{q'p'})(1+n^o_{q''p''})}{\omega_{\mathbf{q}p}\omega_{\mathbf{q}'p'}\omega_{\mathbf{q}''p''}}\\&\times\delta(\omega_{\mathbf{q}p}-\omega_{\mathbf{q}'p'}-\omega_{\mathbf{q}''p''})\mathcal{R}^-_{\mathbf{q}p,\mathbf{q}'p',\mathbf{q}''p''},\end{aligned}\tag{9}$$

where N is the total number of atoms in the crystal and the factor $\mathcal{R}^{\pm}$ depends on the polarization vectors and the potential derivatives [see Eq. (26) in I]. If we consider also the presence of isotope scattering centers in the lattice, a third term of the following form:

$$\sum_{\mathbf{q}'p'}Q^{\mathbf{q}'p'}_{\mathbf{q}p}[\Psi_{\mathbf{q}'p'}-\Psi_{\mathbf{q}p}]\tag{10}$$

has to be added in the right-hand side of Eq. (7). The probability rate for the isotope scattering is

$$\begin{aligned}Q^{\mathbf{q}'p'}_{\mathbf{q}p}={}&\frac{\pi}{2N}f\left(\frac{\Delta M}{M}\right)^2\omega_{\mathbf{q}p}\omega_{\mathbf{q}'p'}n^o_{qp}(1+n^o_{q'p'})\\&\times|\mathbf{e}^*_{\mathbf{q}p}\cdot\mathbf{e}_{\mathbf{q}'p'}|^2\delta(\omega_{\mathbf{q}'p'}-\omega_{\mathbf{q}p}),\end{aligned}\tag{11}$$

where f is the fraction of unit cells having a difference of mass ΔM.[11]

Since the present approach avoids the use of the relaxation time approximation for three-phonon scattering processes, a rigorous description of the interference effects between these collisions and Rayleigh scattering due to point impurities is provided.

Let us introduce an auxiliary function ψ related to the deviation phonon function Ψ by the following relation:

$$\Psi_{\mathbf{q}p}=-\sum_i\psi_{\mathbf{q}p,i}\nabla_iT,\tag{12}$$

the index i denoting the i component of a Cartesian reference frame. The iterative solution of the Boltzmann equation is the limit $n\rightarrow\infty$ of the function generated by the following recurrence relation:

$$\begin{aligned}\psi^{n+1}_{\mathbf{q}p,i}={}&\frac{k_BTv_{\mathbf{q}p,i}}{\mathcal{Q}_{\mathbf{q}p}}\frac{\partial n^o_{qp}}{\partial T}+\frac{1}{\mathcal{Q}_{\mathbf{q}p}}\sum_{\mathbf{q}'p'}Q^{\mathbf{q}'p'}_{\mathbf{q}p}\psi^n_{\mathbf{q}'p'}\\&+\frac{1}{\mathcal{Q}_{\mathbf{q}p}}\left\{\sum_{\mathbf{q}'p',\mathbf{q}''p''}Q^{\mathbf{q}''p''}_{\mathbf{q}p,\mathbf{q}'p'}[\psi^n_{\mathbf{q}''p''}-\psi^n_{\mathbf{q}'p'}]\right.\\&\left.+\frac{1}{2}\sum_{\mathbf{q}'p',\mathbf{q}''p''}Q^{\mathbf{q}'p',\mathbf{q}''p''}_{\mathbf{q}p}[\psi^n_{\mathbf{q}''p''}+\psi^n_{\mathbf{q}'p'}]\right\},\end{aligned}\tag{13}$$

where

$$\begin{aligned}\mathcal{Q}_{\mathbf{q}p}={}&\sum_{\mathbf{q}'p',\mathbf{q}''p''}Q^{\mathbf{q}''p''}_{\mathbf{q}p,\mathbf{q}'p'}+\frac{1}{2}\sum_{\mathbf{q}'p',\mathbf{q}''p''}Q^{\mathbf{q}'p',\mathbf{q}''p''}_{\mathbf{q}p}\\&+\sum_{\mathbf{q}'p'}Q^{\mathbf{q}'p'}_{\mathbf{q}p}.\end{aligned}\tag{14}$$

III. COMPARISON WITH EXPERIMENTAL DATA

After the iterative solution of Eq. (13), the heat current density

$$\mathbf{U}=\frac{1}{\Omega}\sum_{\mathbf{q}p}\hbar\omega_{\mathbf{q}p}\mathbf{v}_{\mathbf{q}p}n_{\mathbf{q}p}=-\frac{1}{\Omega}\sum_{\mathbf{q}p}\hbar\omega_{\mathbf{q}p}\mathbf{v}_{\mathbf{q}p}\frac{\partial n^o_{qp}}{\partial(\hbar\omega_{\mathbf{q}p})}\Psi_{\mathbf{q}p}\tag{15}$$

can be easily evaluated. Ω is the crystal volume. With respect to a Cartesian reference frame, the n component of the current is

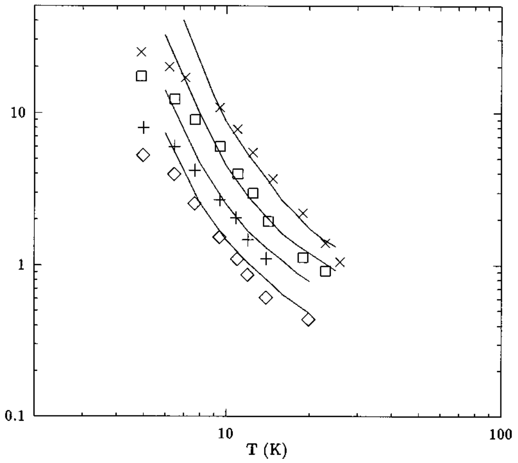

FIG. 2. Thermal conductivity (in $\mathrm{W\,m^{-1}\,K^{-1}}$) for neon as a function of temperature along several isocores. The experimental points are from Weston and Daniels (Ref. 5): ◇ ($13.35\ \mathrm{cm^3/mole}$), + ($12.66\ \mathrm{cm^3/mole}$), □ ($11.95\ \mathrm{cm^3/mole}$), × ($11.16\ \mathrm{cm^3/mole}$).

$$U_n = -\sum_i \kappa_{ni} \nabla_i T, \tag{16}$$

where

$$\kappa_{ni} = \frac{\hbar \Phi^2}{16\pi^3 m v k_B T^2} \sum_p \int_{\mathrm{BZ}} d^3\eta \frac{e^{b\overline{\omega}_p}}{(e^{b\overline{\omega}_p}-1)^2} \overline{\omega}_p \frac{\partial \overline{\omega}_p}{\partial \eta_n} \mathcal{F}_{pi} \tag{17}$$

is the thermal conductivity tensor. The integral substitutes a sum over $\mathbf{q}$ in the first Brillouin zone (BZ). In Eq. (17), an adimensional wave vector $\boldsymbol{\eta}$ and a reduced frequency $\overline{\omega}$ are used. $\boldsymbol{\eta}$ is linked to $\mathbf{q}$ by the relation $\mathbf{q} = 2\pi\sqrt{2}\,\boldsymbol{\eta}/h_1$ and $\overline{\omega}$ to the phonon frequency by $b\overline{\omega} = \hbar\omega/(k_B T)$ with

$$b = \frac{\hbar}{h_1 k_B T} \left(\frac{\Phi}{2m} \right)^{1/2}. \tag{18}$$

The function $\mathcal{F}_{pi}$ is connected to the deviation function by the following relation:

$$\Psi_{\mathbf{q}p} = -\frac{\Phi h_1^4}{8\pi^2 v T} \sum_i \mathcal{F}_{pi} \nabla_i T, \tag{19}$$

where v is the cell volume $v = \Omega/N$.

For calculating the functions $\mathcal{F}_{pi}$, a crucial step is the choice of the number $\mathcal{N}$ of points one uses to sample the BZ: the procedure to determine the best choice has been previously explained. As in I we use for the calculation $\mathcal{N} = 7488$, which ensures the convergence of the iteration procedure.

The behavior of the thermal conductivity as a function of the temperature is shown in Fig. 2 in comparison with the experimental data of Weston and Daniels.[5] The experimental data are obtained at constant volume conditions: in the iterative calculation the nearest-neighbor distance h_1 is also kept constant and its value is taken by the relation $h_1 = (\sqrt{2}v)^{1/3}$ from the cell volume v directly obtained from the experimental molar volume v_m.

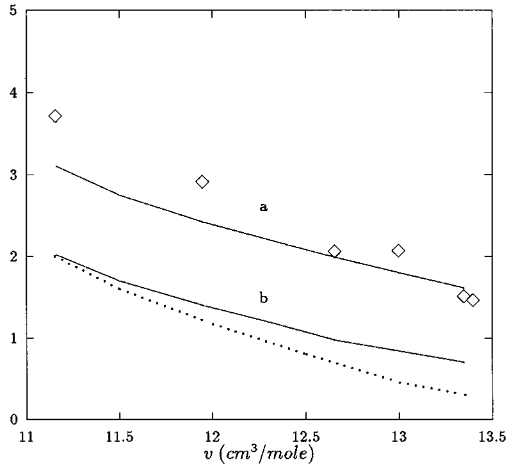

FIG. 3. Thermal conductivity (in $\mathrm{W\,m^{-1}\,K^{-1}}$) for neon as a function of the molar volume at the reduced temperature $T/\Theta_0 = 1/8$. Curve a is obtained by means of the effective, and curve b by the bare Lennard-Jones potential. The dotted line represents the prediction of Julian's theory. The experimental points are from Weston and Daniels (Ref. 5), from Clemans (Ref. 6), and Kimber and Rogers (Ref. 19).

One of the samples prepared and studied by Weston and Daniels ($v_m = 13.35\ \mathrm{cm^3/mole}$) has nearly the same lattice spacing a ($a = 4.460$ Å) of the sample studied by Endoh *et al.* ($a = 4.466$ Å) (see Fig. 1 for the phonon energies).

At low temperature, the effects of grain boundaries and dislocations become relevant and the theoretical curves, which do not include these effects, deviate from the experimental data.

To appreciate the agreement between the experimental and the iterative data, let us consider the behavior of the conductivity as a function of the volume at constant reduced temperature: this is shown by curve a in Fig. 3. Like Weston and Daniels,[5] let us choose for the reduced temperature the value of $T/\Theta_o = 1/8$, where the thermal conductivity is dominated by the umklapp processes for all the neon samples. For the Debye temperatures Θ_o, we used that reported in Ref. 5: 75.78, 86.58, 100.08, 118.82 K for the samples with molar volumes 13.35, 12.66, 11.95, and 11.16 $\mathrm{cm^3/mole}$, respectively.

In the same figure, the prediction of Julian's theory[18] is reported for comparison. In doing the comparison, it is necessary to remember that the result of Julian's calculation is obtained without considering the isotopic effect that is instead considered in the present iterative approach. The effect of the mass difference is to decrease the conductivity: in Table I the thermal conductivities of an isotopically pure sample in comparison with the natural sample are given.

TABLE I. Thermal conductivity of natural and isotopically pure neon, κ_n and κ_p in $\mathrm{W\,m^{-1}\,K^{-1}}$ for different molar volume (in $\mathrm{cm^3/mole}$) at different temperatures.

T (K)	κ_n ($v_m = 11.16$)	κ_p ($v_m = 11.16$)	κ_n ($v_m = 13.35$)	κ_p ($v_m = 13.35$)
10	8.77	9.58	1.46	1.70
20	1.83	2.03	0.48	0.55

From the table, one can see that the isotopic effect is slightly higher in the sample with larger molar volume. The effects of additional scattering from force-constant changes and local strain field are not considered here.

In Fig. 3, the result of the iterative calculation done with the bare Lennard-Jones potential (curve *b*) is also shown: the comparison between curves *a* and *b* reveals that the choice of the potential is fundamental.

Due to the lack of arbitrariness in the iterative procedure, from the obtained results we can achieve that the potential used by Young for calculating the thermodynamical properties of neon is able to describe the thermal conductivity, too.

A concluding observation on the effective potential can be obtained from Fig. 3: since higher volumes correspond to lower reduced temperatures, the effective potential seems to work better at low temperature. The agreement is, however, good.

IV. CONCLUSION

The iterative approach is a numerical but rigorous approach that gives good agreement with the experimental data not only, as it was already verified, in the case of argon and krypton, but also for the lighter of the rare-gas solids, that is neon. The choice of an effective Lennard-Jones potential, which takes into account the quantum effects of the zero-point motion, proves to be fundamental in the calculation. The iterative method is then a good tool for checking the potential parameters from the thermal conductivity measurements.

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