Phonon Scattering by the F-Center Electron

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The scattering of phonons by the electron bound to the F center has been calculated using conventional perturbation theory. The process is analogous to the scattering of light from an atom, with the electron making virtual transitions to an excited state. In this case it is found that the most important transitions are to a level lying above the first excited state. It is found that the scattering rate initially follows a Rayleigh law, being proportional to ω^4, where ω is the phonon frequency. However, as ω becomes larger than about half the Debye frequency, the scattering becomes weaker. Using the results of this calculation it has been possible to account for most of the experimentally observed effect of F centers on the thermal conductivity.

I. INTRODUCTION

IN considering the interaction between the F center and the vibrations of the host lattice, the scattering by the electron has been ignored. It was felt that the electron was very tightly bound and thus any interaction between it and the lattice vibrations would be negligible.[1] It is the purpose of this communication to investigate this point in some detail, and it will be found that the scattering of the higher frequency phonons can in fact be appreciable.

The electronic wave functions are coupled to those for the lattice through a term[2]

$$V_{\mathrm{eL}}(\psi)(\Phi), \tag{1}$$

where ψ and Φ are the electronic and ionic wave functions, respectively. This term is neglected when ψ and Φ are determined in the adiabatic approximation. We will use it as the interaction potential in a conventional perturbation theory calculation of the scattering.

Because the energy gap between the ground and excited states is of the order of a few electron volts, and phonon energies are of the order of 10^{-2} eV, we need not consider first-order processes. Our problem will then consist of calculating the elastic scattering in second order. The large difference between the energy gap and the phonon energies also permits us to ignore any resonance effects.

Formally the problem is identical to that for the scattering of light from an atom.[3] In practice our problem is also very similar to the scattering of phonons from electrons in shallow impurity levels in the semiconductors which has been treated by Keyes,[4] and in somewhat greater detail by Griffin and Carruthers.[5] There is, however, one important difference: the size of the electronic orbit is much smaller in the case of the F center, and the electron can be considered as being almost entirely confined to the vacancy. Therefore

instead of calculating V_{eL} in the deformation potential approximation, as was done for the semiconductors, we consider only the F electron's interaction with its nearest neighbors. We will also confine our attention to the alkali halides with the NaCl structure. We will follow the usual practice and take the change in the potential energy of the F-center electron upon displacement of the surrounding ions for V_{eL}.[2] Furthermore we will simplify the problem by only considering the Coulomb interaction with the nearest neighbors, and since we are interested in comparing our results with experimental data on the low-temperature lattice thermal conductivity we will only consider the scattering of the acoustical modes.

The Coulomb field in which the F-center electron finds itself is a relatively sensitive function of the positions of the six nearest neighbors. It appears that it is most sensitive to the separation between the nearest neighbors, i.e., to the volume of the box in which the electron finds itself. Thus we will ignore the effect of shearing displacements of the surrounding ions and confine our attention to the effect of changes in separation between the nearest-neighbor ions taken in opposing pairs. Thus the scattering of the transverse modes can probably be safely neglected and we need only consider the interaction with longitudinal mode. Our interaction potential, then, will be of the form[2]

$$V_{\mathrm{eL}}=\sum_{m}(\partial U/\partial u_m)u_m, \tag{2}$$

where we are simply adding to contributions of the six nearest neighbors, and where u_m is the displacement of the nearest-neighbor atom and U is the potential energy of the electron.

Our task then is to calculate a relaxation time which will then be used to compute a conductivity. This is the single-mode relaxation time[6] defined by[5]

$$1/\tau_{qt}=\sum_{q't'} W(qt \rightarrow q't'), \tag{3}$$

where τ_{qt} is the relaxation time of a mode of wave vector q and polarization t, and $W(qt \rightarrow q't')$ is a transition probability. In computing the transition proba-

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[1] R. O. Pohl, Phys. Rev. **118**, 1499 (1960).

[2] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, Oxford, 1960), p. 179.

[3] W. Heitler, *The Quantum Theory of Radiation* (Oxford University Press, Oxford, 1954).

[4] R. W. Keyes, Phys. Rev. **122**, 1171 (1961).

[5] A. Griffin and P. Carruthers, Phys. Rev. **131**, 1976 (1963).

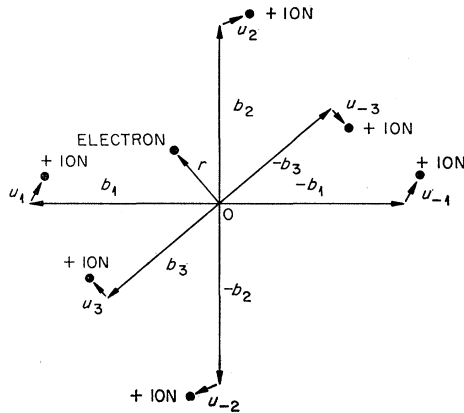[6] P. Carruthers, Rev. Mod. Phys. **33**, 101 (1961).

FIG. 1. Relationship between nearest neighbors and
F-center electron.

bility we will require the second-order matrix elements for two cases:

(a) phonon qt is absorbed with the electron making a transition to the intermediate state, then the electron returns to the ground state and phonon $q't'$ is emitted;

(b) phonon $q't'$ is emitted first and then phonon qt is absorbed.

These are the only two possibilities which need be considered: Since the energy gap is also large compared with KT, the number of electrons initially in the excited state is negligible. Therefore we need not consider the scattering from electrons in the excited state.

Having obtained the matrix elements for the two cases we shall then proceed to calculate the relaxation time using the Debye approximation. Unfortunately, we will be interested in values of the wave vector large enough for the Debye approximation to be very bad. However, at the present time we have no choice and must use it if the problem is to be at all tractable.

In calculating the matrix elements we will find that transitions from the ground to the first excited state (corresponding to the F band) are relatively unimportant. Our major concern will be with transitions from the ground state to another spherically symmetric state whose energy places it just above the level of the first excited state. It appears that electronic transitions to this state lead to the K band. Information on this and other higher excited states has recently become available.[7] We will, however, be concerned only with the first of these, and will ignore scattering due to transitions to the higher levels.

For this reason and because of the other uncertainties that plague this type of calculation our results should be viewed with some caution. We will find, however, that they do suggest that a mechanism of this sort can lead to a scattering of phonons which is of

sufficient magnitude to appreciably affect the thermal conductivity.

II. THE RELAXATION TIME

We take for our interaction potential the change in the potential energy experienced by the F electron on displacement of the nearest-neighbor ions. This is[8]

$$\Delta V = \frac{-e^2}{|\mathbf{b}_m - (\mathbf{r} + \mathbf{u}_m)|} + \frac{e^2}{|\mathbf{b}_m - \mathbf{r}|}, \qquad (4)$$

where b_m is the vector from the center of the vacancy to the ion at m, r is the vector to the electron, and u_m is the displacement of the ion. If we expand the right-hand side we obtain, keeping the first three terms:

$$\Delta V = -e^2 \left[\frac{\mathbf{b}_m \cdot \mathbf{u}_m}{a_0^3} \right] - e^2 \left[\frac{3(\mathbf{b}_m \cdot \mathbf{r})(\mathbf{b}_m \cdot \mathbf{u}_m)}{a_0^5} - \frac{\mathbf{r} \cdot \mathbf{u}_m}{a_0^3} \right]$$
$$- \frac{15}{2} e^2 \left[\frac{(\mathbf{b}_m \cdot \mathbf{r})^2 (\mathbf{b}_m \cdot \mathbf{u}_m)}{a_0^7} - \frac{3(\mathbf{b}_m \cdot \mathbf{r}_m)(\mathbf{r}_m \cdot \mathbf{u}_m)}{a_0^5} \right], \qquad (5)$$

where $a_0 = |b_m|$. We have also eliminated all terms in second and higher powers of $\mathbf{u}_m$ since their contribution is negligible compared to those linear in $\mathbf{u}_m$.

The first term in the expansion does not couple the electron to the lattice and is of no interest. The second term is linear in the electronic coordinates and can induce transitions between electronic states of different parity. The contribution of this term to the scattering, however, is less than that due to the terms which can couple states of the same parity. We will summarize a calculation of the scattering due to the term linear in r in an Appendix. We now proceed with the calculation of the scattering due to the term in r^2.

Summing the contributions of the six nearest neighbors, the interaction becomes (see Fig. 1)

$$-\frac{e^2}{a_0} \left[\frac{15}{2} \frac{(\mathbf{b}_1 \cdot \mathbf{r})^2 \mathbf{b}_1 \cdot (\mathbf{u}_1 - \mathbf{u}_{-1})}{a_0^6} - 3\frac{(\mathbf{b}_1 \cdot \mathbf{r}) \mathbf{r} \cdot (\mathbf{u}_1 - \mathbf{u}_{-1})}{a_0^4} \right.$$
$$+ \frac{15}{2} \frac{(\mathbf{b}_2 \cdot \mathbf{r})^2 \mathbf{b}_2 \cdot (\mathbf{u}_2 - \mathbf{u}_{-2})}{a_0^6} - 3\frac{(\mathbf{b}_2 \cdot \mathbf{r}) \mathbf{r} \cdot (\mathbf{u}_2 - \mathbf{u}_{-2})}{a_0^4}$$
$$+ \frac{15}{2} \frac{(\mathbf{b}_3 \cdot \mathbf{r})^2 \mathbf{b}_3 \cdot (\mathbf{u}_3 - \mathbf{u}_{-3})}{a_0^6} - 3\frac{(\mathbf{b}_3 \cdot \mathbf{r}) \mathbf{r} \cdot (\mathbf{u}_3 - \mathbf{u}_{-3})}{a_0^4} \right]. \qquad (6)$$

We write the displacement of an ion at b_m as

$$\mathbf{u}_m = \sum_{\mathsf{q},t} \left(\frac{\hbar}{2\rho V \omega_{\mathsf{q},t}} \right)^{1/2} \boldsymbol{\varepsilon}_{\mathsf{q},t} (a_{\mathsf{q},t} + a_{\mathsf{q},t}^*) e^{i\mathsf{q} \cdot \mathbf{b}_m}, \qquad (7)$$

where ρ is the density and V is the volume of the crystal; ω is the frequency, q the wave vector, and ϵ the polariza-

[7] R. F. Wood, Phys. Rev. Letters 11, 202 (1963).

[8] J. M. Conway, D. A. Greenwood, J. A. Krumhansl, and W. Martienssen, Phys. Chem. Solids 24, 239 (1963).

tion vector of the wave; a_q and a_q^* are annihilation and creation operators, respectively.

Substituting and taking rectangular coordinate axes through the nearest-neighbor equilibrium positions:

$$V_{\text{eL}} = \sum_{q,t} \left(\frac{\hbar}{2\rho V \omega_{q,t}}\right)^{1/2} (a_{q,t} + a_{qt}{}^*) \frac{-e^2}{a_0{}^4}$$

$$\times [9\epsilon_x x^2 \sin a_0 q_x - 6x(\epsilon_y y \sin a_0 q_x + \epsilon_z z \sin a_0 q_x)$$

$$+9\epsilon_y y^2 \sin a_0 q_y - 6y(\epsilon_x x \sin a_0 q_y + \epsilon_z z \sin a_0 q_y)$$

$$+9\epsilon_z z^2 \sin a_0 q_z - 6z(\epsilon_x x \sin a_0 q_z + \epsilon_y y \sin a_0 q_z)]. \quad (8)$$

The terms in xy, xz, and yz yield zero when the electronic matrix elements are computed. Hence,

$$V_{\text{eL}} = \sum_{q,t} \frac{-9e^2}{a_0{}^4} \left(\frac{\hbar}{2\rho V \omega_{q,t}}\right)^{1/2} (a_{q,t} + a_{q,t}{}^*)$$

$$\times (x^2 \epsilon_x \sin a_0 q_x + y^2 \epsilon_y \sin a_0 q_y + z^2 \epsilon_z \sin a_0 q_z). \quad (9)$$

Using this potential we wish to calculate a transition probability

$$W(q, t \rightarrow q', t') = (2\pi/\hbar) |K_{q,q'}|^2 \delta(\hbar\omega_q - \hbar\omega_{q'}). \quad (10)$$

In this expression $K_{q,q'}$ is the sum of two second-order matrix elements: the first corresponds to the absorption of q and the emission of q'; the second, to the emission of q' followed by the absorption of q. Thus

$$K_{q,q'} = \left[\frac{\langle(n_{q'}+1)(n_q-1)\psi_{\text{gd}}| V_{\text{eL}} |(n_{q'})(n_q-1)\psi_{\text{exc}}\rangle\langle(n_{q'})(n_q-1)\psi_{\text{exc}}| V_{\text{eL}} |(n_{q'})(n_q)\psi_{\text{gd}}\rangle}{E_{\text{exc}} - E_{\text{gd}} + \hbar\omega_q}\right]$$

$$+ \left[\frac{\langle(n_{q'}+1)(n_q-1)\psi_{\text{gd}}| V_{\text{eL}} |(n_{q'}+1)(n_q)\psi_{\text{exc}}\rangle\langle(n_{q'}+1)(n_q)\psi_{\text{exc}}| V_{\text{eL}} |(n_{q'})(n_q)\psi_{\text{gd}}\rangle}{E_{\text{exc}} - E_{\text{gd}} + \hbar\omega_q}\right]. \quad (11)$$

Since $\hbar\omega_q \ll \Delta E = E_{\text{exc}} - E_{\text{gd}}$,

$$K_{q,q'} \cong 2\frac{n_q{}^{1/2}(n_{q'}+1)^{1/2}}{\Delta E}(\Gamma)^2 A (\sin a_0 q)(\sin a_0 q'), \quad (12)$$

where

$$\Gamma = \langle\psi_{\text{exc}}| r_i{}^2 |\psi_{\text{gd}}\rangle \quad (13)$$

and

$$A = \frac{\hbar}{2\rho V \omega_{q,t}}\left(\frac{9e^2}{a_0{}^4}\right)^2. \quad (14)$$

In this expression we have specialized the interaction to a phonon traveling in the $\langle 100\rangle$ direction. For this case the transverse modes do not lead to any interaction, and only the longitudinal mode need be considered. Actually it is possible to carry the calculation through and evaluate the appropriate angular averages. However this is difficult to do correctly, particularly for phonons at the boundaries of the Brillouin zone. Since other assumptions such as the isotropy of the velocity of sound, and the Debye approximation will prove necessary, the more correct angular averages probably do not warrant the additional labor. Actually these have been computed approximately and it was found that they did not change the results of the calculation. This is not surprising considering the high degree of symmetry in the NaCl lattice.

The results of this calculation will be compared with experimental data on thermal conductivity. This will be accomplished in the relaxation time approximation using the approach due to Callaway.[9] Thus we require the single mode relaxation time, defined as

$$\frac{1}{\tau_q} = N_F \sum_{q'} \frac{W(q, t \rightarrow q', t')}{n_q(n_{q'}+1)}, \quad (15)$$

where N_F is the number of F centers in the crystal.

We now replace the sum by an integral in the usual fashion, assume a Debye spectrum, and we have neglected any anisotropy in the velocity of sound. With the δ function the integration over q is easily done, and we have ignored the angular variation of $K_{q,q'}$, thus:

$$\frac{1}{\tau_q} = \frac{N_F V}{(2\pi)^3} \int \frac{W(q, t \rightarrow q', t')}{n_q(n_{q'}+1)}(dq)^3, \quad (16)$$

$$\frac{1}{\tau_q} = \frac{n_f}{\pi C^3}\left(\frac{1}{\rho \Delta E}\right)\left(\frac{\Gamma \times 9e^2}{a_0{}^4}\right)^4 (\sin a_0 q)^4, \quad (17)$$

which is our final result, and in which n_f is now the number of F centers per unit volume, and C is the velocity of sound.

III. COMPARISON WITH EXPERIMENT

Unfortunately the experimental situation with regard to the effect of F centers on the thermal conductivity is not clear. Apparently the difficulty is associated with defects which are introduced together with the F centers. Recent work by Walker[10] shows, for instance, a marked difference between additively colored crystals and those in which the defects have been introduced through irradiation. As Walker points out, however, it appears that the most successful way of introducing F centers with a minimum of other defects is by additive coloration. Walker has measured the change in thermal conductivity upon additive coloration only in KCl, and we will compare the results of our calculation with his data. We will not consider his results for irradiated

[9] J. Callaway, Phys. Rev. 113, 1046 (1959).

[10] C. T. Walker, Phys. Rev. 132, 1963 (1963).

crystals because of the probable presence of other defects whose effect cannot be taken into account.

In attempting to deduce defect scattering laws from thermal conductivity data the following procedure is used[11]: Experimental data are obtained for the pure crystal and for the crystal plus defects. The pure crystal curve is matched (often somewhat arbitrarily) using laws for scattering from the crystal boundaries, umklapp and normal processes and residual impurities and defects likely to be found in the crystal. Then, to the scattering terms for the pure crystal, a term is added appropriate to the defect introduced and one attempts to reproduce the curve for the crystal plus defect. In our case the defect scattering law we wish to compare with experiment is the one deduced in the previous section. Thus we will add this to the terms with which Walker was able to reproduce his pure crystal curve and attempt to reproduce the curves he obtained for his additively colored crystals. We will immediately find that we cannot reproduce the results at temperatures below the maximum. However, as Walker points out, it is likely that his crystals contain colloids, and that these are responsible for the additional depression in the conductivity at the lowest temperatures. Thus in addition to the terms for the pure crystal we will also use an additional term for the scattering due to the colloids. This turns out to be simply an additional boundary scattering term. Therefore our attention will be focused on the effect of the F centers at temperatures near the maximum.

Before we can estimate the magnitude of the scattering term we have calculated, we must estimate the electronic matrix element. To do this we require the electronic wave functions appropriate to the two levels we will be concerned with. These have been calculated for LiCl by Wood[12] and are available only for this substance. However, it appears that in the alkali halides the wave functions for the F electron are all similar, differing only in a scale factor which is proportional to the lattice spacing. This is, of course, not strictly true, but is an adequate approximation for our purposes. Thus we will use the LiCl function and simply scale the result to obtain the matrix element for KCl. For LiCl the wave functions are

$$\psi_{gd} = \psi_{2s} = N_{2s}\left[\left(\frac{\beta^5}{3\pi}\right)^{1/2} re^{-\beta r} - 0.0645 \sum_{i=1}^{6} \Phi_i\right], \quad (18)$$

$$\psi_{exc} = N[\psi_{3s} - \langle 3s/2s\rangle\psi_{2s}], \quad (19)$$

[11] C. T. Walker and R. O. Pohl, Phys. Rev. 131, 1433 (1963).

[12] These wave functions have been obtained by the LCAO method and are a rather complicated combination of 2s and 2p orbitals centered on the neighboring Li ions. The functions which we shall use are simple vacancy centered approximations supplied by Dr. Wood. While it is not yet absolutely clear that the K band should be associated with a transition between the states considered here there is little doubt that a level whose wave function was the same symmetry as the ground state lies near the first excited state.

where

$$\psi_{3s} = N_{3s}\left[\left(\frac{2\beta'^7}{45\pi}\right)^{1/2} r^2 e^{-\beta' r} - 0.0309 \sum_{i=1}^{6} \Phi_i\right]. \quad (20)$$

The values of the numerical constants are $N = N_{2s} = N_{3s} \cong 1$, $\beta = 0.75$, $\beta' = 0.30$, and $\langle 3s/2s\rangle = 0.30223$. Using these wave functions we obtain for LiCl, $\Gamma = 2.70$ (a.u.)^2.

If we assume that β and β' are simply inversely proportional to a_0, this becomes $\Gamma = 0.117a_0^2$, and our expression for the relaxation time reduces to

$$\frac{1}{\tau_q} = \frac{n_f}{\pi C^3}\left(\frac{1}{\rho\Delta E}\right)^2\left(\frac{1.05e^2}{a_0^2}\right)^4 (\sin a_0 q)^4. \quad (21)$$

For the value of ΔE in this equation we shall use the energy corresponding to the K-band transition. In KCl this is 2.71 eV. For the other constants we have, in mks units, $n_f = 10^{24} \text{m}^{-3}$, $C = 3.15 \times 10^3 \text{m/sec}$, $a_0 = 3.14 \times 10^{-10}\text{m}$, $e = 1.6 \times 10^{-19}\text{C}$, $\rho = 1984 \text{ kg/m}^3$, $\Delta E = 4.34 \times 10^{-19}\text{J}$.

Substitution of these in Eq. (21) yields

$$1/\tau_q = 5 \times 10^8 (\sin a_0 q)^4 \text{ sec}^{-1}. \quad (22)$$

It is now necessary to translate the results of our calculation into a change in the thermal conductivity. To do this we substitute our expression for the relaxation time into Callaway's formula for the conductivity

$$K = \left(\frac{kT}{\hbar}\right)^3 \int_0^{\theta/T} \frac{x^4}{\sum 1/\tau(x)} \frac{e^x}{(e^x-1)^2} dx, \quad (23)$$

where $x = \hbar\omega/kT$ and in our case the sum of the relaxation times for the pure crystal becomes

$$\sum 1/\tau(x) = BT^4 x^4 + C'T^3 e^{-a/T} + D, \quad (24)$$

where the first term accounts for isotopic and residual impurity scattering, the second for umklapp processes, and the third for boundary scattering.

For the crystal plus F centers we use

$$\sum 1/\tau(x) = BT^4 x^4 + C'T^3 x^2 e^{-a/T} + D' + E(\sin bTx)^4. \quad (25)$$

In this expression we simply continue the Debye approximation so that $b = \pi/\theta$, i.e., $bTx = \pi$ when $x = \theta/T$. We also use an increased boundary term to obtain agreement with the data at the lowest temperatures.

This integral has been evaluated numerically (and agreement with experiment was obtained) for the following values of the constants: $B = 33$ (°K)$^{-4}$ sec^{-1}, $C' = 5 \times 10^4$ (°K)$^{-3}$ sec^{-1}, $D = 5.8 \times 10^5$ sec^{-1}, $D' = 12 \times 10^5$ sec^{-1}, $E = 1.5 \times 10^9$ sec^{-1}, $a = 40$°K, $\theta = 232$°K. The results are shown in Figs. 2 and 3.

The value of E necessary for agreement between theory and experiment is a factor of 3 higher than that calculated. However, this discrepancy is not serious

being well within the probable error associated with the calculations.

IV. DISCUSSION

It appears that the mechanism we have considered here can account satisfactorily for the experimental data available on the effect of F centers on the thermal conductivity. It is also possible, however, as Walker has done, to account for the data using a point-defect scattering law (such that the relaxation time is inversely proportional to the fourth power of the phonon frequency), and a resonant scattering from a quasilocal mode. However, what is possibly most important, is that this calculation shows that the mechanism we have considered should be able to make a significant contribution to the scattering. This mechanism not only provides a scattering which initially is proportional to ω^4, but the fact that the scattering becomes weaker for phonons approaching the zone boundary (i.e., as a_0q approaches π) reproduces some of the features of the "resonance dip."

We have not reproduced the experimental data exactly. However, the theoretical and experimental curves are close enough for the agreement to be considered adequate, considering the approximations we have made. Probably the most serious of these is the neglect of dispersion. If dispersion were taken into account, qualitatively one would find that the scattering would increase as the velocity of sound decreased. Thus, for phonons of low frequency, the scattering would be less than for those of high frequency. Since the low-frequency phonons are important at the lower temperatures, the conductivity would tend to be enhanced at the lower temperatures and diminished at the higher tempera-
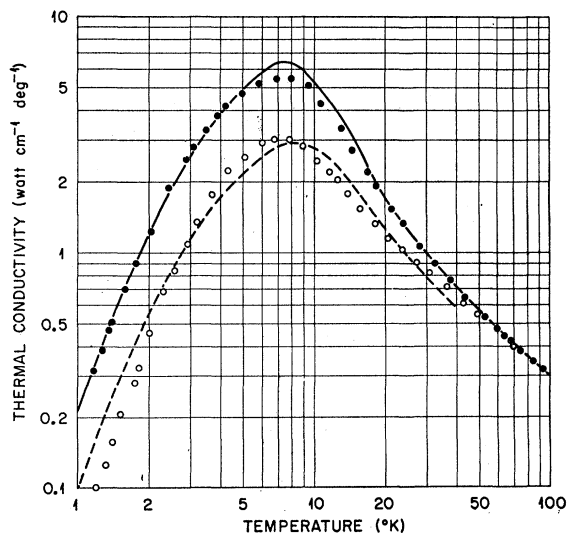

FIG. 2. Comparison between calculated curve (broken line) and Walker's experimental points (open circles) for additively colored and quenched KCl.
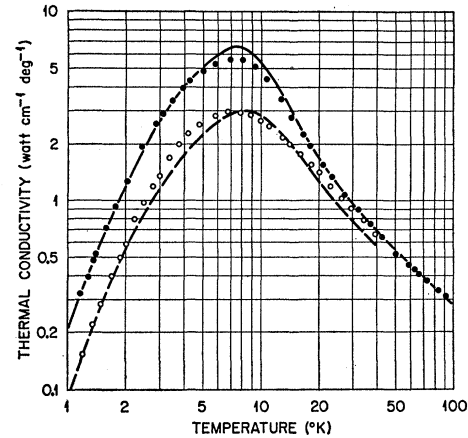

FIG. 3. Comparison between the same calculated curve as Fig. 2, and Walker's experimental points for slowly cooled KCl.

tures. This would tend to shift the maximum to a lower temperature and to bring theory and experiment into better agreement.

At this point it would be well to summarize the other assumptions we have found necessary:

(a) We have neglected the effect of the other ions in the crystal. However, the results of two crude attempts to take them into account reveal that this assumption is probably alright. Their effect was considered in two ways: The first consisted of replacing the ions by concentric spheres of uniform charge. The total charge on each sphere was made equal to the sum of the charges on all the ions whose distance from the F center equaled the radius of the sphere. Then the effect of all the spheres was summed out to the twentieth sphere. The second consisted of calculating the detailed interaction for a phonon traveling in a $\langle 100 \rangle$ direction with the ions on concentric cubes around the F center. The interaction of the electron with the ions on cubes whose sides were $2a_0$, $4a_0$, $6a_0$, and $8a_0$ were then added.

(b) We have specialized our interaction to a phonon traveling in the $\langle 100 \rangle$ direction. However, we have in fact calculated the appropriate angular average, and find that its use does not yield a conductivity which differs at any temperature by more than 5%.

(c) We have neglected the other excited states of the F center. This has proved necessary because wave functions for these states were not available. Unfortunately one could anticipate a large correction if these were taken into account. However, the corrections would be only to the strength of the scattering, and not to the functional dependence on phonon wave vector: In general, one may expect to obtain two kinds of interaction potential, one of odd parity, and the other of even parity. On adding the effect of the two opposing nearest-neighbor ions for the case of odd parity we find that the interaction potential yields a function $(\cos a_0q - 1)$ for a $\langle 100 \rangle$ phonon. Upon suitable manipu-

lation (see the Appendix) one obtains a scattering law which is proportional to $(\cos a_0 q-1)^4$. Upon expanding the cosine function we find the scattering initially is proportional to $(a_0 q)^8$ and is considerably weaker than the one obtained using the interaction of even parity which will yield a function $(\sin a_0 q)^4$.

(d) We have used an expansion of the Coulomb interaction in which we have neglected certain terms of higher order, in d and r. The terms of higher order in d can safely be neglected since they occur in powers of the ratio (d/a_0). However, the terms of higher order in r cannot be disposed of quite as safely, and the possibility exists that they may contribute to the calculated relaxation time. But again for the reasons outlined in Sec. c one expects that the effect will be to change the strength of the scattering, not its functional dependence on phonon wave vector.

(e) There is one more correction to the calculation which has not been taken into account: When we write the Hamiltonian for the imperfect crystal, we find we must substract a term corresponding to the missing ion, i.e.,

$$H_{\text{imp}}=H_{\text{perfect}}+H_{F\text{ center}}-H_{\text{Cl}^-}.$$

Thus we should substract from our matrix elements the corresponding terms which refer to the missing ion. In this case the electronic transition we would be interested in would be transition to exciton levels. However, the energy denominators for these transitions are of the order of three times as large, and we would expect the matrix elements to be small enough so that their neglect is not serious. For this reason we would also not expect this mechanism to be important in the case of the scattering of phonons by an impurity atom.

To summarize then, we feel reasonably confident that our scattering function is of the right form. It is not as certain, however, that the calculated magnitude is reliable. Nevertheless, it is probably safe to say that even this feature of the calculation is probably no more uncertain than any of the other defect scattering laws derived in the literature.

ACKNOWLEDGMENTS

APPENDIX

The second term in the expansion (5), linear in r, can lead to transition between the ground state and the first excited state. In this case the interaction potential is (7) in our notation:

$$V_{\text{eL}}=\frac{e^2}{a_0}\left[\frac{3(\mathbf{b}_1\cdot\mathbf{r})\mathbf{b}_1\cdot(\mathbf{u}_1+\mathbf{u}_{-1})}{a_0^4}-\frac{\mathbf{r}\cdot(\mathbf{u}_1+\mathbf{u}_{-1})}{a_0^2}\right.$$
$$+\frac{3(\mathbf{b}_2\cdot\mathbf{r})\mathbf{b}_2\cdot(\mathbf{u}_2+\mathbf{u}_{-2})}{a_0^4}-\frac{\mathbf{r}\cdot(\mathbf{u}_2+\mathbf{u}_{-2})}{a_0^2}$$
$$\left.+\frac{3(\mathbf{b}_3\cdot\mathbf{r})\mathbf{b}_3\cdot(\mathbf{u}_3+\mathbf{u}_{-3})}{a_0^4}-\frac{\mathbf{r}\cdot(\mathbf{u}_3+\mathbf{u}_{-3})}{a_0^2}\right]$$

which, with Eq. (7) leads to

$$V_{\text{eL}}=eF_x x-eF_y y-eF_z z,$$

where

$$F_i=\frac{2e}{a_0^3}\sum_{q,t}\left(\frac{\hbar}{2\rho V\omega_{qt}}\right)^{1/2}(a_{qt}+a_{qt}{}^*)$$
$$\times[2\cos q_i a_0-\cos q_j a_0-\cos q_k a_0].$$

Specializing to a phonon traveling in the x, or $\langle 100\rangle$ direction,

$$V_{\text{eL}}=\frac{4e^2}{a_0^3}\sum_{q,t}\left(\frac{\hbar}{2\rho V\omega_{qt}}\right)^{1/2}(a_{qt}+a_{qt}{}^*)[\cos a_0 q-1].$$

Now, following the steps indicated in Eqs. (9) through (17) we find that

$$1/\tau_q=A'(\cos a_0 q-1)^4.$$

If we expand the cosine function we find that $1/\tau_q$ is initially proportional to $(a_0 q)^8$. It can be appreciated that the magnitude of the term A' is of the same order as that of A, Eq. (14). Therefore the scattering due to this process will be smaller by a factor of about $(a_0 q)^4$, and can be neglected.