

Electronic Energy Transfer via Virtual-Phonon Processes

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A model is presented for transfer of electronic energy between impurity ions in a solid, via virtual-phonon processes. When the energy being transferred is much greater than the maximum phonon energy in the solid, the transfer rate varies approximately as R^{-6} for electric dipole, and as R^{-10} for electric-quadrupole transitions of the impurity ions, where R is the range between the impurities. One difference between our treatment and that of Orbach and Tachiki, in which an exponential range dependence is obtained, is that our electron-lattice coupling involves distant, not just nearest, neighbors. These results apply when no local modes are present. Local modes produce additional effects which, under certain conditions, dominate strongly over band-mode contributions to energy transfer.

I. INTRODUCTION

THE principal mechanism that has been proposed for the transfer of electronic excitation between impurity ions in a crystal involves the direct Coulomb interaction between the charge configurations of the ions.^{1,2} Dexter's theory of this mechanism treats this interaction in terms of a multipole expansion of the charge configurations: The lowest-order contribution involves the interaction between the electric-dipole moments of the two ions; higher-order contributions involve electric-dipole-electric-quadrupole interactions, etc.

In this paper we discuss an alternate energy-transfer mechanism, viz., the virtual-phonon exchange mechanism. In this case coupling between ions occurs through an indirect process: Each impurity ion is coupled to the lattice through the interaction between its electrons and the charges on the lattice ions. This interaction influences both the electronic states and the motion of the lattice. Hence, the electrons on one impurity ion perturb the lattice which in turn perturbs the electrons on the second impurity. This amounts to a coupling between the electrons on separated ions. The theoretical expression of this effect involves a second-order perturbation process in which virtual phonons are emitted (or absorbed) at the excited ion and absorbed (emitted) at the relaxed ion site. This will be more thoroughly discussed in Sec. II.

This mechanism was first proposed by Sugihara³ for the coupling of spins of paramagnetic ions in a crystal, and it was further developed by Aminov and Kochelaev⁴ and by McMahon and Silsbee.⁵ Orbach and Tachiki⁶ extended the theory to the problem of electronic energy transfer in cases where the transferred energy Δ is much

greater than the maximum phonon energy of the crystal $\hbar\omega_c$. They found that in this limit the energy-transfer rate drops off exponentially with impurity separation, the exponent being proportional to $\ln(\Delta/\hbar\omega_c)$. They concluded that the virtual-phonon mechanism could be important in the case of ruby, compared with Dexter's electric quadrupole-quadrupole mechanism,^{6,7} when the Cr^{3+} ions are nearest- or next-nearest neighbors. We find that the exponential range dependence is a consequence of their model for the electron-lattice interaction in which coupling is assumed to take place only between the impurity ions's electrons and the nearest-neighbor lattice ions. If this simplifying feature of the model is removed, the range dependence is found to be approximately inverse power laws where the power of range depends on the nature of the electronic transition. Further, these power-law dependences closely match the range dependences of the corresponding electric multipole-multipole mechanisms of Dexter. We also find that the existence of local modes can, under certain conditions, increase energy transfer by several orders of magnitude. The effect of local modes was not previously considered. A temperature dependence is also found for the virtual-phonon mechanism, but this appears to be small for typical cases.

In Sec. II we describe the model used in the calculations and discuss significant assumptions made. Section III contains a derivation of the electron-lattice interaction in which an impurity ion electron is influenced by all of the lattice ions. Electron-electron coupling in the perfect lattice is worked out in Sec. IV, and the effects of local modes are considered in Sec. V.

II. MODEL AND SIGNIFICANT ASSUMPTIONS

The analysis presented here is based on a one-dimensional model of the lattice. With this model it is possible to obtain analytic expressions for all effects studied. (Calculations are in progress for a three-dimensional lattice and preliminary results are substantially the same as for the one-dimensional case.) The lattice is taken to be infinitely long with periodic boundary conditions applied over a period of N ions; motion of the

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¹ F. Perrin, *J. Phys. Radium* **7**, 1 (1936); Th. Förster, *Ann. Physik* **2**, 55 (1948).

² D. L. Dexter, *J. Chem. Phys.* **21**, 836 (1953).

³ K. Sugihara, *J. Phys. Soc. (Japan)* **14**, 1231 (1959).

⁴ L. K. Aminov and B. I. Kochelaev, *Zh. Eksperim. i Teor. Fiz.* **42**, 1301 (1962) [English transl.: *Soviet Phys.—JETP* **15**, 903 (1962)].

⁵ D. H. McMahon and R. H. Silsbee, *Phys. Rev.* **135**, A91 (1964).

⁶ R. Orbach and M. Tachiki, *Phys. Rev.* **158**, 524 (1967).

⁷ G. F. Imbusch, *Phys. Rev.* **153**, 263 (1967).

ions is along the direction of the lattice. The lattice ions are spaced a distance a apart in their equilibrium positions, have mass M , and carry alternating positive and negative charges. Hence, each lattice site is a center of inversion symmetry. Two identical impurity ions of mass M' are placed at positive ion sites at $\pm d$ lattice units from the origin. (This symmetric placement of the impurities is convenient but not necessary; the final results are independent of the choice of origin.) It is assumed that the electronic wave functions of the impurities do not overlap.

In the energy-transfer process the initial state of the system consists of one of the ions being in an excited state and the other being in its ground state. Energy transfer occurs if the excited ion relaxes while the second ion becomes excited. We consider only the case where the difference of energy Δ between the ground and excited states of an ion is much greater than the maximum phonon energy $\hbar\omega_c$. In this limit it is very improbable that the energy will be transferred by the excited ion giving its energy to the lattice and the second ion subsequently becoming excited by absorbing energy from the lattice. Hence, it is necessary that both ions change their states simultaneously. We are excluding direct interactions between impurity ions so there is no term in the interaction Hamiltonian containing products of operators of different impurities. Therefore, the interaction cannot change the states of both ions in first-order perturbation theory. This can occur in second order, however. When, as in the present case, no matrix element exists between the initial state l and the final state n , of the system, the transition probability involves $|\mathcal{H}_{ln}^{(2)}|^2$,⁸ where

$$\mathcal{H}_{ln}^{(2)} = \sum_m \frac{V_{lm}V_{mn}}{E_{mn}}.$$

Here the sum is over all available intermediate states of the system, E_{mn} is the energy difference between the final (or initial) and intermediate states, and the V_{ij} are matrix elements of the interaction Hamiltonian. In this case the transition occurs through a virtual intermediate state in which one ion's state is changed, to the final state in which both ions's states are changed. The intermediate states must differ from the initial and final states by the addition or subtraction of one or more phonons in one or more modes; the intermediate state for which the lattice state is unchanged gives no contribution to the transfer probability. These added or subtracted phonons in the intermediate, virtual, states are referred to as virtual phonons. We consider the interacting impurities to be in exact resonance so that the initial and final states of the lattice must be the same, as required by energy conservation.

III. ELECTRON-LATTICE INTERACTION

The potential energy of an electron on the i th impurity ion due to the other ions in the lattice is given by the following expression:

$$V_i(r_i, \theta_i, \varphi_i) = \frac{e}{K_e} \sum_{l=0}^{\infty} \sum_{m=-l}^l (1-\sigma_l) \beta_{lm} r_i^l Y_{lm}(\theta_i, \varphi_i), \quad i=1, 2 \quad (1)$$

where

$$\beta_{lm} = -\left(\frac{4\pi e}{2l+1}\right) \sum_j \frac{\eta_j}{R_{ij}^{l+1}} Y_{lm}(\Theta_j, \Phi_j) \quad (R_{ij} > r_i).$$

Here e is the electronic charge; K_e is the dielectric constant of the lattice (we will neglect the dependence of K_e on range between the lattice ions and the impurities, and its dependence on frequency); $(r_i, \theta_i, \varphi_i)$ are the spherical coordinates of the electron on the i th impurity; and $(R_{ij}, \Theta_j, \Phi_j)$ are the coordinates of the j th lattice ion with respect to the i th impurity. Taking the polar axes of the nuclear and electronic coordinate systems along the lattice permits us to set $m=0$ in (1). Since the lattice ions move along the lattice, the Y 's can be replaced by 1 for ions, say, on the right-hand side of the impurity and ± 1 for those on the left-hand side.

The σ_l are shielding factors for the active electron, against the l th term of the crystal field,⁹ due to other electrons on the ion. The degree of shielding depends, of course, on the type of orbital involved, e.g., f orbitals on rare-earth ions will be shielded more for lower values of l than d orbitals on the same ions. Hence, in such cases as Ce^{3+} the ground state, in which the electron is in an f orbital, will be shielded to a different degree than the excited state, in which the electron is in a d orbital.

The effective charge on the j th ion is $e\eta_j$, where η_j will depend on the degree of covalent bonding.

The electron-lattice coupling expressed in Eq. (1) contains the influence of all lattice ions on the impurity electron, rather than only nearest neighbors as in the Orbach-Tachiki analysis. Inclusion of the long-range electron-lattice interaction was prompted, in part, by the work of Koningstein¹⁰ where it was shown that distant ions make an important contribution to the crystal field at an impurity ion. Hence, it appeared proper to include long-range interactions in our analysis.

In this analysis, only the terms for $l=1, 2$ are considered because these are the first odd- and the first even-parity electronic terms and contain all the salient features of the interaction. The higher-order terms are of small importance for orbitals having a mean radius much smaller than the lattice constant a , since the magnitude of the p th term relative to the magnitude of the term for $l=1$ is roughly $(\langle r \rangle / 2ad)^{p-1}$, where $2ad$

⁹ R. M. Sternheimer, M. Blume, and R. F. Peierls, Phys. Rev. **173**, 376 (1968).

¹⁰ J. A. Koningstein, in *Optical Properties of Ions in Crystals*, edited by H. M. Crosswhite and H. W. Moos (Wiley-Interscience, Inc., New York, 1967), p. 105.

⁸ L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Co., New York, 1955), p. 201.

is the separation between the impurities. For the 4f orbitals of the rare earths, the contribution of the next higher odd or even term to the energy-transfer matrix element will be on the order of $3 \times 10^{-3}/d^2$ of the lowest odd or even term; for d orbitals the contribution will be on the order of $3 \times 10^{-2}/d^2$ of the lowest-order term. (It should be remembered, however, that this argument is based on the point-charge model for the lattice.) If the bonding is covalent, terms in the lattice potential for $l > 1, 2$ can be important when the impurities are near neighbors.

If the magnitude of the charges on negative and positive ions are taken to be the same, then (1) becomes

$$V_i = \text{const} + \alpha_{10} r_i Y_{10}(\theta_i, \varphi_i) \sum_{j=1}^{\infty} (-1)^j \left[\frac{1}{R_{i+j}^2} - \frac{1}{R_{i-j}^2} \right] \\ + \alpha_{20} r_i^2 Y_{20}(\theta_i, \varphi_i) \sum_{j=1}^{\infty} (-1)^j \left[\frac{1}{R_{i+j}^3} + \frac{1}{R_{i-j}^3} \right] \\ + \text{higher-order terms in } (r_i/R_{i\pm j}), \quad (2)$$

where

$$\alpha_{10} = \frac{-4\pi e^2 \eta (1 - \sigma_l)}{(2l+1)K_e},$$

and

$$R_{i\pm j}^{-s} = [ja \pm (U_{i\pm j} - U_i)]^{-s}. \quad (3)$$

Here ja is the equilibrium position of the j th ion with respect to the origin and U_j is the displacement of the ion from its equilibrium position. Expanding (3) and retaining only terms linear in the U 's gives the lowest-order contribution to the electron-lattice interaction [the lowest-order terms in V are the static crystal field, which is obtained from (2) and (3) by setting the U 's equal to 0; however, this does not contribute to the energy-transfer process]

$$V_i' = -\frac{2\alpha_{10}}{a^3} r_i Y_{10}(\theta_i, \varphi_i) \\ \times \sum_{j=1}^{\infty} \frac{(-1)^j}{j^3} [(U_{i+j} - U_i) + (U_{i-j} - U_i)] \\ - \frac{3\alpha_{20}}{a^4} r_i^2 Y_{20}(\theta_i, \varphi_i) \\ \times \sum_{j=1}^{\infty} \frac{(-1)^j}{j^4} [(U_{i+j} - U_i) - (U_{i-j} - U_i)], \quad i = \pm d. \quad (4)$$

It will be shown in Sec. IV that V_i' yields an expression for energy transfer which is independent of temperature. The second term in the expansion of (2), V_i'' , is quadratic in the U 's and is temperature-dependent. In addition to the question of temperature dependence of the energy-transfer process, we are concerned with the convergence of the expansion of V_i . The relative

magnitude of V_i' and V_i'' will give a criterion for the validity of considering only the first one or two terms in this expansion. V_i'' is given by the quadratic terms in the U 's in the expansion of (3):

$$V_i'' = \frac{3\alpha_{10}}{a^4} r_i Y_{10}(\theta_i, \varphi_i) \\ \times \sum_{j=1}^{\infty} \frac{(-1)^j}{j^4} [(U_{i+j} - U_i)^2 - (U_{i-j} - U_i)^2] \\ + \frac{6\alpha_{20}}{a^5} r_i^2 Y_{20}(\theta_i, \varphi_i) \\ \times \sum_{j=1}^{\infty} \frac{(-1)^j}{j^5} [(U_{i+j} - U_i)^2 + (U_{i-j} - U_i)^2]. \quad (5)$$

It is shown below that the contribution of V_i'' to the transfer probability will be small compared to that of V_i' for reasonable values of a , ω_e , and M .

The U 's in V_i' and V_i'' can be expressed in a phonon representation by use of the expansion

$$U_j = \left(\frac{\hbar}{2MN} \right)^{1/2} \sum_k \omega_k^{-1/2} (a_k e^{ikx_j} + a_k^+ e^{-ikx_j}), \quad (6)$$

where a_k and a_k^+ are annihilation and creation operators for phonons of wave number k and frequency ω_k , and x_j is the equilibrium position of the j th lattice ion. The summation over k is restricted to the N points in the first Brillouin zone. It is sufficient for computational purposes to simply substitute (6) into (4) and (5) and thereby obtain operators V_i' and V_i'' in the phonon representation. Instead of doing this, we will express V_i' and V_i'' in a way which makes the symmetry of the phonon parts of the operation explicit. Denoting the k th Fourier component of $(U_{i\pm j} - U_i)$ in (6) by $D_{i\pm j}(k)$, we define the operators $S_j^{(i)}(k)$ and $A_j^{(i)}(k)$ as follows:

$$S_j^{(i)}(k) = \frac{1}{2} [D_{i+j}(k) - D_{i-j}(k)], \quad (7a)$$

$$A_j^{(i)}(k) = \frac{1}{2} [D_{i+j}(k) + D_{i-j}(k)]. \quad (7b)$$

These are, therefore, operators for the k th Fourier component of even and odd motion, respectively, of the ions at $\pm ja$, relative to the i th impurity ion. Using (6) in (7a) and (7b) yields

$$S_j^{(i)}(k) = i \left(\frac{\hbar}{2MN\omega_k} \right)^{1/2} [a_k e^{ikx_i} - a_k^+ e^{-ikx_i}] \\ \times \sin(kja), \quad (8a)$$

$$A_j^{(i)}(k) = -2 \left(\frac{\hbar}{2MN\omega_k} \right)^{1/2} [a_k e^{ikx_i} + a_k^+ e^{-ikx_i}] \\ \times \sin^2(\frac{1}{2}kja), \quad (8b)$$

where $x_1 = -da$ and $x_2 = +da$.

Finally, using (6)–(8) in (4) and (5) gives

$$\begin{aligned}
 V_i' &= \frac{-4\alpha_{10}}{a^3} r_i Y_{10}(\theta_i, \varphi_i) \sum_k \sum_{j=1}^{\infty} \frac{(-1)^j}{j^3} A_j^{(i)}(k) \\
 &\quad + \frac{-6\alpha_{20}}{a^4} r_i^2 Y_{20}(\theta_i, \varphi_i) \sum_k \sum_{j=1}^{\infty} \frac{(-1)^j}{j^4} S_j^{(i)}(k), \quad (9) \\
 V_i'' &= \frac{12\alpha_{10}}{a^4} r_i Y_{10}(\theta_i, \varphi_i) \sum_{k,k'} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^4} S_j^{(i)}(k) A_j^{(i)}(k') \\
 &\quad + \frac{6\alpha_{20}}{a^5} r_i^2 Y_{20}(\theta_i, \varphi_i) \sum_{k,k'} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^5} [S_j^{(i)}(k) S_j^{(i)}(k') \\
 &\quad + A_j^{(i)}(k) A_j^{(i)}(k')]. \quad (10)
 \end{aligned}$$

The order of operators in (10) is unimportant because the commutator $[a_k, a_{k'}^+] = \delta_{kk'}$ gives no contribution to the matrix element for energy transfer. It is seen that V_i' and V_i'' have odd-parity electronic operators associated with odd motion of the symmetrically placed neighbors about the i th impurity and even electronic operators associated with even lattice motion. This is, of course, a consequence of the inversion symmetry of the impurity sites, which requires that the over-all symmetry of the interaction Hamiltonian be even. Thus, only phonon functions with odd inversion symmetry about the impurity are active in energy transfer if the ion's electronic state changes parity and only even symmetry phonon functions are active if parity does not change. Orbach and Tachiki consider only the even motions of a symmetric lattice about an impurity ion, and their results therefore hold only for the case where the electronic transitions involve no change in parity. The one-dimensional equivalent of their results will be derived as a special case in Sec. IV.

It is apparent that V_i' connects states of the lattice which differ by one phonon in any one of the normal modes, while V_i'' affects two phonons at a time.

IV. ENERGY TRANSFER WITH PERFECT LATTICE MODES

In this section we assume that the character of the normal modes of the lattice is not altered by the presence of the impurity ions, i.e., the effects of local modes or modified band modes are neglected. These effects are considered in Sec. V. We take the zero-order states of the electron-phonon system to be the following:

$$|p, p'; n_1, n_2 \dots n_N\rangle = \psi_p(\mathbf{r}_1) \psi_{p'}(\mathbf{r}_2) |n_1, n_2 \dots n_N\rangle, \quad (11)$$

where p and p' are the sets of quantum numbers which specify the electronic states of the first and second impurity ions. It is assumed here that the electronic wave functions of the two ions do not overlap. Taking the two impurity ions to be in exact resonance, the states of the system before and after energy transfer differ only in that

the quantum numbers of the two ions are interchanged. The initial and final states of the lattice are identical in this case. For V_i' , the intermediate states, discussed in Sec. II, can be any of the following:

$$\begin{aligned}
 &|p, p; n_1, \dots, n_q \pm 1, \dots, n_N\rangle, \\
 &|p', p'; n_1, \dots, n_q \pm 1, \dots, n_N\rangle. \quad (12)
 \end{aligned}$$

Taking all of these intermediate states into account (see Appendix A) gives the following results:

$$\begin{aligned}
 \mathcal{H}_e'^{(2)}(R) &= \frac{64\hbar^2\alpha_{10}^2}{MN a^6} |\langle p | r Y_{10} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^3} \\
 &\quad \times \sum_k \frac{\cos(kR) \sin^2(\frac{1}{2}kj'a) \sin^2(\frac{1}{2}kj'a)}{\Delta_{pp'}^2 - (\hbar\omega_k)^2}, \quad (13)
 \end{aligned}$$

$$\begin{aligned}
 \mathcal{H}_e''^{(2)}(R) &= \frac{36\hbar^2\alpha_{20}^2}{MN a^8} |\langle p | r^2 Y_{20} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^4} \\
 &\quad \times \sum_k \frac{\cos(kR) \sin(kj'a) \sin(kj'a)}{\Delta_{pp'}^2 - (\hbar\omega_k)^2}, \quad (14)
 \end{aligned}$$

where $\Delta_{pp'}$ is the energy of the electronic transition and $R=2da$ is the distance between the impurities. The subscripts o and e correspond to the cases where electronic parity does and does not change in the transition $p \rightarrow p'$, respectively. At this point we can obtain the one-dimensional equivalent of Orbach and Tachiki's (OT) results by setting $j=j'=1$ in $\mathcal{H}_e'^{(2)}$, i.e., by considering only nearest neighbors in the electron-lattice coupling. Assuming the dispersion law $\omega_k^2 = \omega_c^2 \sin^2(\frac{1}{2}ka)$ and replacing summation by integration through

$$\sum_k \Rightarrow \frac{Na}{2\pi} \int_{-\pi/a}^{\pi/a} dk$$

gives

$$\begin{aligned}
 [\mathcal{H}_e'^{(2)}]_{\text{OT}} &= \text{const} \\
 &\quad \times \int_{-\pi/a}^{\pi/a} \frac{\cos(kR) \sin^2(ka) dk}{\Delta_{pp'}^2 - [\hbar\omega_c \sin(ka/2)]^2}. \quad (15a)
 \end{aligned}$$

For $\Delta_{pp'} > \hbar\omega_c$, the integrand of (15a) can be expanded in a power series in $(\hbar\omega_c/\Delta)$ and the integration can be carried out term by term (see Ref. 6 for further details). The final result is an $\mathcal{H}_e'^{(2)}$ which varies exponentially with distance between the impurity ions:

$$|\mathcal{H}_e'^{(2)}|_{\text{OT}} = \text{const} \times \left(\frac{\hbar\omega_c}{2\Delta} \right)^{2R/a}, \quad \frac{\hbar\omega_c}{2\Delta} \Delta_{pp'} \gg \hbar\omega_c. \quad (15b)$$

This result can be obtained directly from Orbach and Tachiki's work by setting $e^x = e^y = k_x = k_y = 0$, $e^z = 1$, $k_z = k$ in their Eq. (3) and then using this result in their (5). Hence, our analysis is completely consistent with theirs if only nearest-neighbor electron-lattice interactions are considered. It should also be emphasized that this exponential range dependence is obtained only with the particular phonon dispersion law assumed. If

ω_k is taken to be constant, e.g., as an approximation to an optical phonon branch, the Orbach-Tachiki analysis gives $\mathcal{H}_e'^{(2)} = 0$ for $R > 2a$. This difficulty is not present when the influence of distant ions on the impurity ion electron is considered. In the limit $\Delta_{pp'} \gg \hbar\omega_c$, $\hbar\omega_k$ can be ignored in (13) and (14) without affecting the results significantly. When this is done the integrals can be easily evaluated and the following results are obtained:

$$\begin{aligned} \mathcal{H}_o'^{(2)}(R) &= \frac{-4\hbar^2\alpha_{10}^2}{Ma^6\Delta_{pp'}^2} |\langle p | r Y_{10} | p' \rangle|^2 \\ &\quad \times \left\{ \frac{3.6a^3}{R^3} + \sum_{j=1}^{\infty} \frac{1}{j^3(R/a+j)^3} \right. \\ &\quad \left. + \sum_{j=1}^{(R/a-1)} \frac{1}{j^3(R/a-j)^3} \right\}, \quad (16) \\ \mathcal{H}_e'^{(2)}(R) &= \frac{-9\hbar^2\alpha_{20}^2}{Ma^8\Delta_{pp'}^2} |\langle p | r^2 Y_{20} | p' \rangle|^2 \\ &\quad \times \left\{ \sum_{j=1}^{\infty} \frac{1}{j^4(R/a+j)^4} - \sum_{j=1}^{(R/a-1)} \frac{1}{j^4(R/a-j)^4} \right\}, \\ &\quad \Delta_{pp'} \gg \hbar\omega_c. \quad (17) \end{aligned}$$

The quantities within the curly brackets, which we refer to as G_o and G_e , are shown in Fig. 1. These results are

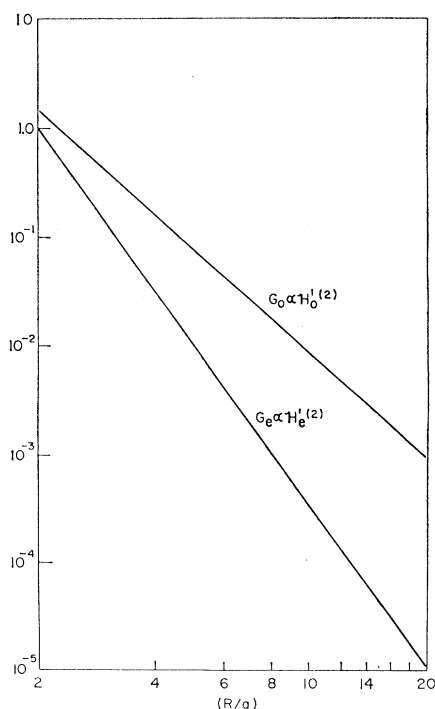


FIG. 1. Dependence of the "perfect lattice" energy-transfer matrix elements on impurity separation R .

accurately approximated by the following expressions:

$$\mathcal{H}_o'^{(2)}(R) \approx -\frac{48\hbar^2\alpha_{10}}{Ma^6\Delta_{pp'}^2} |\langle p | r Y_{10} | p' \rangle|^2 \left(\frac{a}{R}\right)^3, \quad (18)$$

$$\mathcal{H}_e'^{(2)}(R) \approx -\frac{2.9 \times 10^2 \hbar^2 \alpha_{20}^2}{Ma^8\Delta_{pp'}^2} |\langle p | r^2 Y_{20} | p' \rangle|^2 \left(\frac{a}{R}\right)^5, \quad R \geq 2a. \quad (19)$$

Hence, the effect of including interactions of electrons with distant ions is to make the electron-electron interaction long-ranged. In fact, the range dependences of the "odd" and "even" cases are approximately the same as the inverse third and the inverse fifth-power laws for Dexter's electric dipole-dipole and electric quadrupole-quadrupole mechanisms, respectively.

It should be mentioned that the power-law range dependences of $\mathcal{H}_{e,o}'^{(2)}$ are not related to the canceling power-law terms in the Orbach-Tachiki analysis. In that case the contributions to $\mathcal{H}_{e,o}'^{(2)}$ from longitudinal modes and from transverse modes each have a power law term; these terms cancel when the contributions from the various modes are summed and only the exponential range dependence remains. It so happens that there are no such power-law terms in the one-dimensional case when only nearest-neighbor electron-lattice interactions are considered. This is seen from Eq. (15b), which is the one-dimensional equivalent of the Orbach-Tachiki result. Hence, the power-law range dependences shown in (18) and (19) are the result of the long-range electron-lattice interactions. Similar power-law range dependences are found for the three-dimensional case when long-range electron-lattice interactions are considered.

If $\hbar\omega_k$ is not neglected in these calculations, additional terms are obtained; the n th of these is of order $(\hbar\omega_c/\Delta_{pp'})^{2n}$. Since we assume that $\Delta_{pp'} \gg \hbar\omega_c$, these terms are negligible and $\hbar\omega_k$ can be neglected without affecting the results significantly.

The electronic matrix elements involved in Dexter's electric dipole-dipole and quadrupole-quadrupole mechanisms are the same as for the odd and even virtual-phonon exchange mechanisms, respectively, and the matrix elements for energy transfer for these cases, $\mathcal{H}_{dd}(R)$ and $\mathcal{H}_{qq}(R)$ can be written approximately as follows^{2,6}:

$$\mathcal{H}_{dd}(R) \approx \frac{e^2}{K_e R^3} |\langle p | r Y_{10} | p' \rangle|^2 (1 - \sigma_d)^2,$$

$$\mathcal{H}_{qq}(R) \approx \frac{24\pi e^2}{5K_e R^5} |\langle p | r^2 Y_{20} | p' \rangle|^2 (1 - \sigma_q)^2,$$

where σ_d and σ_q are shielding factors for dipole and quadrupole moments: The outer electrons of a rare-earth ion will shield the fields of a moment involving inner orbitals just as they shield against the crystal

field. This shielding acts twice in the direct Coulomb interaction, once in each of the interacting ions, so that direct coupling is reduced by a factor $(1-\sigma)^2$. The ratios of virtual phonon to electrostatic matrix elements are as follows:

$$\left| \frac{\mathcal{H}_o'^{(2)}}{\mathcal{H}_{dd}} \right| \approx \frac{50\eta^2[1-\sigma_1(p)][1-\sigma_1(p')]}{(M/M_n)K_e a^3 \Delta_{pp'}^2 (1-\sigma_d)^2},$$

$$\left| \frac{\mathcal{H}_e'^{(2)}}{\mathcal{H}_{qq}} \right| \approx \frac{7.2\eta^2[1-\sigma_2(p)][1-\sigma_2(p')]}{(M/M_n)K_e a^3 \Delta_{pp'}^2 (1-\sigma_q)^2}.$$

Here M_n is the mass of a nucleon, a is the lattice constant in Å, and $\Delta_{pp'}$ is in eV. Thus, the virtual-phonon mechanism will be most important in cases where the lattice ions are light, highly charged, and close together and when the energy transferred is small. If, for example, $a=2$ Å, $M/M_n=20$, $\eta=3$, $K_e=3.0$, and assuming that

$\sigma_1 \approx \sigma_d$ and $\sigma_2 \approx \sigma_q$, then $|\mathcal{H}_o'^{(2)}/\mathcal{H}_{dd}| \approx 1/\Delta_{pp'}^2$ and $|\mathcal{H}_e'^{(2)}/\mathcal{H}_{qq}| \approx 0.15/\Delta_{pp'}^2$. Hence, for this example $|\mathcal{H}_o'^{(2)}/\mathcal{H}_{dd}| \gtrsim 1$ for $\Delta_{pp'} \lesssim 1$ eV and $|\mathcal{H}_e'^{(2)}/\mathcal{H}_{qq}| \gtrsim 1$ for $\Delta_{pp'} \lesssim 0.39$ eV. It is shown in Sec. V that local modes can increase the transfer probability in the odd case (dipole-dipole-like case) by several orders of magnitude so that the virtual-phonon mechanism could be of major importance for less favorable combinations of the values of a , M , η , K_e , and $\Delta_{pp'}$. In particular, generally $\Delta_{pp'} > 1$ eV for the odd case, while there are many even transitions for which $\Delta_{pp'} < 1$ eV.

The contributions of V_i'' to $\mathcal{H}^{(2)}$ will now be considered. Taking the initial state of the lattice to be $|n_1, \dots, n_l, \dots, n_m, \dots, n_N\rangle$, then V_i'' connects this state with the intermediate states $|n_1, \dots, n_{l\pm 1}, \dots, n_{m\pm 1}, \dots, n_N\rangle$, where l and m can take any of the N values. Proceeding as in (13) and (14), we obtain the following contributions to the energy-transfer matrix elements (see Appendix B):

$$\mathcal{H}_o''^{(2)}(R) = \frac{9\alpha_{10}^2(4\hbar)^3 |\langle p | r Y_{10} | p' \rangle|^2}{(a^4 M N \Delta_{pp'})^2} \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^4} \sum_{k,k'} \left[\frac{(n'+\frac{1}{2})}{\omega_{k'}} + \frac{(n+\frac{1}{2})}{\omega_k} \right] \cos kR \cos k'R$$

$$\times \sin(ka j) \sin^2(\frac{1}{2}k'a j) \sin(ka j') \sin^2(\frac{1}{2}k'a j'), \quad (20)$$

$$\mathcal{H}_e''^{(2)}(R) = \frac{9\alpha_{20}^2(4\hbar)^3 |\langle p | r^2 Y_{20} | p' \rangle|^2}{(2a^5 M N \Delta_{pp'})^2} \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^5} \sum_{k,k'} \left[\frac{(n'+\frac{1}{2})}{\omega_{k'}} + \frac{(n+\frac{1}{2})}{\omega_k} \right] \cos(kR) \cos(k'R)$$

$$\times \{ \sin(ka j) \sin(k'a j) \sin(ka j') \sin(k'a j') + 16 \sin^2(\frac{1}{2}ka j) \sin^2(\frac{1}{2}k'a j) \sin^2(\frac{1}{2}ka j') \sin^2(\frac{1}{2}k'a j') \}, \quad (21)$$

where n and n' are the occupation numbers for the normal modes with wave numbers k and k' . To obtain thermally averaged quantities from these expressions, n and n' must be replaced by their mean values \bar{n} :

$$\bar{n} = [\exp(\hbar\omega_k/k_B T) - 1]^{-1}.$$

Using the dispersion law $\omega_k^2 = \omega_c^2 \sin^2(\frac{1}{2}ka)$ and integrating over one of the k variables yields

$$\mathcal{H}_o''^{(2)}(R, T) = \frac{36\alpha_{10}^2 \hbar^3 |\langle p | r Y_{10} | p' \rangle|^2}{\pi a^8 M^2 \Delta_{pp'}^2 \omega_c} \left\{ 4 \left(\frac{a}{R} \right)^4 \sum_{j=1}^{\infty} \frac{(-1)^{j+1}}{j^4} \int_0^{\pi/a} f(k, R, T) \sin(kR) \sin(ka j) dk \right.$$

$$+ \sum_{j=1}^{\infty} \frac{1}{j^4 (R/a + j)^4} \int_0^{\pi/a} f(k, R, T) g(k, R + ja) dk$$

$$\left. - \sum_{j=1}^{(R/a-1)} \frac{1}{j^4 (R/a - j)^4} \int_0^{\pi/a} f(k, R, T) g(k, R - ja) dk \right\}, \quad (22)$$

$$\mathcal{H}_e''^{(2)}(R, T) = \frac{72\alpha_{20}^2 \hbar^3 |\langle p | r^2 Y_{20} | p' \rangle|^2}{\pi a^{10} M^2 \Delta_{pp'}^2 \omega_c} \left\{ 16 \left(\frac{a}{R} \right)^5 \sum_{j=1}^{\infty} \frac{(-1)^{j+1}}{j^5} \int_0^{\pi/a} f(k, R, T) \sin^2(\frac{1}{2}kR) \sin^2(\frac{1}{2}ak j) dk \right.$$

$$+ \sum_{j=1}^{\infty} \frac{1}{j^5 (R/a + j)^5} \int_0^{\pi/a} f(k, R, T) g(k, R + ja) dk$$

$$\left. + \sum_{j=1}^{(R/a-1)} \frac{1}{j^5 (R/a - j)^5} \int_0^{\pi/a} f(k, R, T) g(k, R - ja) dk \right\}, \quad (23)$$

where

$$f(k, R, T) = \frac{(\bar{n}(T) + \frac{1}{2})}{\sin(\frac{1}{2}ka)} \cos(kR),$$

$$g(k, R \pm ja) = [1 + \cos(kR) - \cos(ka) - \cos(k[R \pm ja])].$$

From (16), (17), (22), and (23) we find that

$$|\mathcal{H}_o''^{(2)}/\mathcal{H}_o'^{(2)}| = (\beta/a)^2 |F_o(R, T)/G_o(R)|, \quad (24)$$

$$|\mathcal{H}_e''^{(2)}/\mathcal{H}_e'^{(2)}| = (\beta/a)^2 |F_e(R, T)/G_e(R)|, \quad (25)$$

where $\beta = (\hbar/2M\omega_c)^{1/2}$, which is the rms amplitude of a harmonic oscillator in its ground state. G_o , G_e , $\pi F_o/18$ and $\pi F_e/16$ are the quantities within the curly brackets in (16), (17), (22), and (23), respectively. Figure 2 shows F_o and F_e for several values of $k_B T/\hbar\omega_c$. G_o and G_e are repeated from Fig. 1 for convenience of comparison. It is seen that $\mathcal{H}_o''^{(2)}$ and $\mathcal{H}_e''^{(2)}$ are strongly temperature-dependent and have the approximate range dependences R^{-4} and R^{-5} , respectively. It is also seen from (24), (25), and Fig. 2 that in both cases $\mathcal{H}'^{(2)}$ and $\mathcal{H}''^{(2)}$ can be of comparable magnitude, for moderate temperature, for $(\beta/a)^2 \gtrsim 0.1$. As a rough estimate of the magnitude of $(\beta/a)^2$, consider the following reasonable case: $\omega_c = 5 \times 10^{13}$, $a = 2 \text{ \AA}$, and $M = 20M_n$, where M_n is the mass of a nucleon. For this case $(\beta/a)^2 = 7 \times 10^{-4}$ and \mathcal{H}'' is negligible for normal temperatures. If \mathcal{H}'' were comparable to \mathcal{H}' , then higher-order contributions to \mathcal{H} would probably be important also and

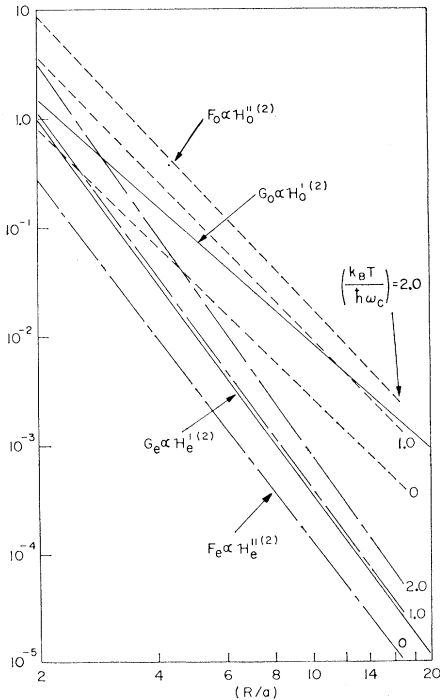


FIG. 2. Temperature-dependent terms in the energy-transfer matrix elements.

the convergence of the expansion of V_i would be uncertain.

Since the impurities are taken to be in exact resonance there are no processes involving crossproducts of V_i' and V_i'' .

V. ENERGY TRANSFER WITH LOCAL LATTICE MODES

Thus far the normal modes of the perfect lattice have been used in calculating the energy-transfer matrix elements. However, if the impurity ion mass or bonds differ from those of the perfect lattice, some very significant changes can occur in the normal modes. If, for example, an impurity is less massive than the lattice ions, then one of the band modes will be replaced by a nonpropagating mode, called a local mode, whose eigenvector decays exponentially with distance from the impurity ion. The amplitude of this mode is $O(1)$, whereas the amplitudes of the $(N-1)$ remaining band modes are $O(N^{-1/2})$. Furthermore, while the frequencies of the band modes are shifted by a negligible amount from their perfect lattice values, the frequency of the local mode can be several times greater than the maximum mode frequency of the perfect lattice. Because of these extraordinary properties, the local mode can have an important effect on energy transfer.

For a single light impurity ion at position d in the one-dimensional lattice, the local-mode frequency $\omega(\text{loc})$ and amplitude $U_j(\text{loc})$ are given by¹¹

$$\omega(\text{loc}) = \omega_c \left(\frac{1}{1 - \epsilon^2} \right)^{1/2}, \quad (26)$$

$$U_j(\text{loc}) = (-1)^{(d+j)} \left(\frac{\hbar}{2M\omega(\text{loc})} \right)^{1/2} \left(\frac{2\epsilon}{1 - \epsilon^2} \right)^{1/2} \left(\frac{1 - \epsilon}{1 + \epsilon} \right)^{|d-j|} \times [a_{10e}^+ + a_{10e}], \quad \text{for } M' < M \quad (27)$$

$$\epsilon = (1 - M'/M),$$

where M' is the impurity ion mass. a_{10e}^+ and a_{10e} are the creation and annihilation operators for the local mode. Since $0 < \epsilon < 1$, the local-mode frequency is greater than the maximum frequency ω_c of the perfect lattice. For two identical light impurities placed at $\pm da$, there are two local modes which have even and odd motion about the origin. The frequencies of these modes are given by the following expressions in the limit $N \gg d$ ¹²:

$$\omega_o = \omega_c \cosh(\frac{1}{2}z_+), \quad (28a)$$

$$\omega_e = \omega_c \cosh(\frac{1}{2}z_-), \quad (28b)$$

¹¹ A. A. Maradudin, in *Phonons and Phonon Interactions*, edited by T. A. Bak (W. A. Benjamin, Inc., New York, 1964), p. 424.

¹² A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), Chap. V.

where the z_{\pm} satisfy

$$\epsilon \coth(\frac{1}{2}z_{\pm}) = 1/(1 \pm e^{-2dz_{\pm}}). \quad (29)$$

It is seen that ω_e and ω_o become equal to $\omega(\text{loc})$ for sufficiently large impurity separations and that they do so more rapidly for larger values of ϵ . This is due to the more rapid exponential decay of the local-mode amplitude with distance from the impurity ion for larger values of ϵ . The amplitudes of the odd and even modes can be approximated well as linear combinations of local-mode amplitudes for single impurities at $\pm da$:

$$U_{j^e, o}(\text{loc}) = \frac{(-1)^{(d+j)}}{\sqrt{2}} \left(\frac{\hbar}{2M\omega_{e, o}} \right)^{1/2} \left(\frac{2\epsilon}{1-\epsilon^2} \right)^{1/2} \times \left[\left(\frac{1-\epsilon}{1+\epsilon} \right)^{|d-j|} \mp \left(\frac{1-\epsilon}{1+\epsilon} \right)^{|d+j|} \right] [a_{e, o^+} + a_{e, o}], \quad (30)$$

where a_{e^+} , a_e are operators for the mode with even inversion symmetry through the origin, etc. The minus sign corresponds to the e and the plus sign corresponds to the o . Using (30) in (4) gives an electron-lattice interaction due to the local modes alone:

$$V_i'(\text{loc}) = \frac{-2\alpha_{10}}{a^3} \left(\frac{\hbar}{2M} \right)^{1/2} \left(\frac{\epsilon}{1-\epsilon^2} \right)^{1/2} r_i V_{10}(\theta_i, \varphi_i) \sum_{j=1}^{\infty} \frac{1}{j^3} \left\{ \frac{1}{(\omega_e)^{1/2}} [B^{R/a+j} + B^{R/a-j} - 2B^j + 2(-1)^j(1-B^{R/a})] (a_{e^+} + a_e) \right. \\ \left. + \frac{1}{(\omega_o)^{1/2}} [B^{R/a+j} + B^{R/a-j} + 2B^j - 2(-1)^j(1+B^{R/a})] (a_{o^+} + a_o) \right\} - \frac{3\alpha_{20}}{a^4} \left(\frac{\hbar}{2M} \right)^{1/2} \left(\frac{\epsilon}{1-\epsilon^2} \right)^{1/2} r_i^2 Y_{20}(\theta_i, \varphi_i) \\ \times \sum_{j=1}^{\infty} \frac{1}{j^4} \left\{ \frac{1}{(\omega_e)^{1/2}} (B^{R/a-j} - B^{R/a+j}) (a_{e^+} + a_e) + (1-2\delta_{i,2}) \frac{1}{(\omega_o)^{1/2}} (B^{R/a-j} - B^{R/a+j}) (a_{o^+} + a_o) \right\}, \quad (31)$$

where $B = [(1-\epsilon)/(1+\epsilon)]$.

Calculations of $\mathcal{H}_e'^{(2)}(\text{loc})$ and $\mathcal{H}_o'^{(2)}(\text{loc})$ are carried out as for (13) and (14). For $\mathcal{H}_e'^{(2)}(\text{loc})$ the contributions of the even and odd modes are additive. Since their frequencies appear in $\mathcal{H}_{e, o}'^{(2)}$ as $1/(\Delta_{pp'}^2 - (\hbar\omega_{e, o})^2)$, and since $\Delta_{pp'} \gg \omega_{e, o}$, no important error is incurred in setting $\omega_e = \omega_o = \omega(\text{loc})$. In the even case, the odd and even local-mode contributions have opposite signs so that setting $\omega_e = \omega_o$ gives $\mathcal{H}_e'^{(2)}(\text{loc}) = 0$ and the difference between ω_e and ω_o must be taken into account to obtain an electron-electron coupling through the local modes. The results of these calculations are

$$\mathcal{H}_e'^{(2)}(\text{loc}) = \frac{32\hbar^2\alpha_{10}^2 |\langle p | r Y_{10} | p' \rangle|^2}{a^6 M \Delta_{pp'}^2} \left\{ \left(\frac{\epsilon}{1-\epsilon^2} \right) \sum_{j, j'=1}^{\infty} \frac{1}{(jj')^3} [B^{R/a+j} + B^{R/a-j} - 2B^{R/a}(-1)^j] [B^{j'} - (-1)^{j'}] \right\}, \\ \mathcal{H}_e'^{(2)}(\text{loc}) = \frac{9\hbar^4\alpha_{20}^2 |\langle p | r^2 Y_{20} | p' \rangle|^2 \omega_o^2}{a^8 M \Delta_{pp'}^4} \left\{ \frac{(\omega_o^2 - \omega_e^2)}{\omega_e^2} \left(\frac{\epsilon}{1-\epsilon^2} \right) \left[\sum_{j=1}^{\infty} \frac{1}{j^4} (B^{R/a-j} - B^{R/a+j}) \right]^2 \right\}. \quad (32)$$

From (16), (17), (31), and (32), the ratios of the local-mode contributions to the unperturbed band mode contributions to \mathcal{H} are found to be

$$|\mathcal{H}_e'^{(2)}(\text{loc})/\mathcal{H}_e'^{(2)}| = |H_o(R, \epsilon)/G_o(R)|, \quad (33)$$

$$|\mathcal{H}_e'^{(2)}(\text{loc})/\mathcal{H}_e'^{(2)}| = \left(\frac{\hbar\omega_e}{\Delta_{pp'}} \right)^2 |H_e(R, \epsilon)/G_e(R)|, \quad (34)$$

where $\frac{1}{8}H_o$ and H_e are the quantities within the curly brackets in (31) and (32). The quantities H_o and H_e are shown in Fig. 3, along with G_o and G_e . It is seen that the local-mode contributions generally strongly dominate the energy-transfer process for the odd case. The local modes are much less important in the even case since $|H_e/G_e| \ll 1$, $(\hbar\omega_e/\Delta) \ll 1$. We therefore conclude that $H_e'^{(2)}(\text{loc})$ can be neglected.

The range dependence of $\mathcal{H}_e'^{(2)}(\text{loc})$ is approximately exponential for small R , with stronger range dependence corresponding to larger values of ϵ . For large R the

range dependence of $\mathcal{H}_e'^{(2)}(\text{loc})$ goes to approximately R^{-3} . It is seen from Fig. 3 that the local-mode contributions to \mathcal{H}_e' are much larger than the perfect band mode contributions for a range of values of ϵ . Since the energy-transfer rate involves $|\mathcal{H}'^{(2)}|^2$, the presence of local modes can increase the transfer rate by several orders of magnitude.

The presence of local modes also reduces the effectiveness of the band modes. This is due to the normalization condition which the normal mode eigenvectors $B_j(k)$ must satisfy at each lattice site:

$$\sum_k M_j B_j^2(k) = 1, \quad (35)$$

where $B_j(k)$ is related to the amplitude of the k th normal mode by

$$U_j(k) = \left(\frac{\hbar}{2\omega_k} \right)^{1/2} B_j(k) [a_k e^{ikx_j} + a_k^+ e^{-ikx_j}]. \quad (36)$$

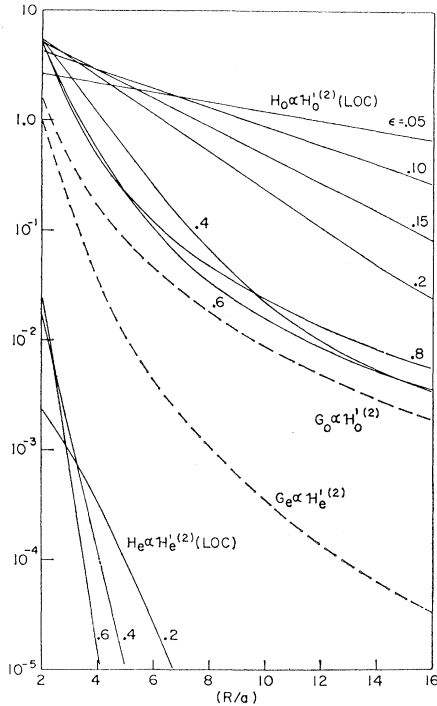


FIG. 3. Local-mode contributions to the energy-transfer matrix elements.

For unperturbed band modes $B_j = 1/(NM)^{1/2}$. For the local modes $k = \pi/a + iz$ and $B_j^{e,o}(\text{loc})$ are the coefficients of $(-1)^{(d+j)}(a_{e,o}^+ + a_{e,o})(\hbar/2\omega_k)^{1/2}$ in (30). The effect of the local modes, through the constraint of normalization, is to reduce the amplitudes of the band modes around the impurity sites. The impurities also destroy the translational invariance of the lattice and change the twofold degenerate plane-wave normal mode of the perfect lattice into nondegenerate standing waves with even and odd inversion symmetry. If the small frequency differences between even and odd band modes and the small shifts in the mode wave numbers are neglected, then the band contribution to the motion of the j th ion can be written as

$$U_j' = \left(\frac{2\hbar}{MN}\right)^{1/2} F(j, \epsilon) \sum_{+k} \omega_k^{-1/2} \{ \cos(kja) \times [A_o(k) + A_o^+(k)] + i \sin(kja) [A_e(k) - A_e^+(k)] \}, \quad (37)$$

where

$$F(j, \epsilon) = \left\{ 1 - \left(\frac{2\epsilon}{1+\epsilon} \right) \left[\left(\frac{1-\epsilon}{1+\epsilon} \right)^{2|d-j|} + \left(\frac{1-\epsilon}{1+\epsilon} \right)^{2|d+j|} \right] \right\}^{1/2}. \quad (38)$$

The creation and annihilation operators for the perturbed even and odd standing wave band modes are

related to the perfect lattice mode operators a_k, a_k^+ as follows:

$$A_o^+(k) = \frac{1}{\sqrt{2}}(a_k^+ + a_{-k}^+), \quad A_o(k) = \frac{1}{\sqrt{2}}(a_k + a_{-k}); \quad (39)$$

$$A_e^+(k) = \frac{1}{\sqrt{2}}(a_k^+ - a_{-k}^+), \quad A_e(k) = \frac{1}{\sqrt{2}}(a_k - a_{-k}).$$

These operators satisfy the usual commutation relations. Using (37) in place of (6) in the calculation of $\mathcal{H}_e'(R)$ and $\mathcal{H}_o'(R)$ gives

$$\mathcal{H}_o^{(2)}(\text{band}) = -\frac{4\hbar^2\alpha_{10}^2}{Ma^6\Delta_{pp'}^2} |\langle p | r Y_{10} | p' \rangle|^2 \left\{ \frac{3.6a^3 F^2(R/2a, \epsilon)}{R^3} + \sum_{j=1}^{\infty} \frac{F^2(R/2a+j, \epsilon)}{j^3(R/a+j)^3} + \sum_{j=1}^{(R/a-1)} \frac{F^2(R/2a-j, \epsilon)}{j^3(R/a-j)^3} \right\}, \quad (40)$$

$$\mathcal{H}_e^{(2)}(\text{band}) = -\frac{9\hbar^2\alpha_{20}^2}{Ma^8\Delta_{pp'}^2} |\langle p | r^2 Y_{20} | p' \rangle|^2 \left\{ \sum_{j=1}^{\infty} \frac{F^2(R/2a+j, \epsilon)}{j^4(R/a+j)^4} - \sum_{j=1}^{(R/a-1)} \frac{F^2(R/2a-j, \epsilon)}{j^4(R/a-j)^4} \right\}. \quad (41)$$

The reduction of $\mathcal{H}_e^{(2)}$ due to the presence of local modes is found to be less than 50% for the odd case and less than 20% for the even case for $0 \leq \epsilon \leq 0.8$.

VI. SUMMARY

Three advances in the theory of the virtual-phonon energy-transfer mechanism are introduced in the present work: (1) the possibility that the parity of an impurity's electronic state changes in the relaxation transition is included in the theory. (2) The electron-lattice coupling is taken to involve every lattice ion, not just the nearest neighbors. (3) The influence of the impurity ions on the crystal's normal modes is considered. In particular, the effects of local modes on energy transfer are studied.

It is shown that, for a symmetric crystal, only lattice modes having even inversion symmetry about an impurity are active in the energy-transfer process if the parity of the ion's electronic state does not change in the relaxation transition; only odd symmetry modes are active if the electronic parity does change. Hence, it is clear that previously obtained results⁶ which include only even modes in the electron-lattice interaction do not hold in cases where electronic parity does change. Among this class are Eu^{2+} and Ce^{3+} where the principal transitions are of the type $4f^n \rightarrow 4f^{n-1}5d$. We have included both odd and even modes in the electron-lattice interaction and we derive energy-transfer prob-

abilities for both parity conserving and parity nonconserving transitions.

The effect of an extensive electron-lattice coupling is particularly important in the limit $\Delta \gg \hbar\omega_e$. If only nearest-neighbor ions are considered in the electron-lattice coupling, then an exponential range dependence for energy transfer can be obtained. This result depends on a particular choice for the phonon dispersion law, however, and a different choice would yield very different results. For example, if the law $\omega_k = \text{const}$ were chosen, the energy-transfer probability would be zero for impurities separated by more than two lattice spaces. When more distant lattice ions are included in the electron-lattice coupling, as in the present work, the analysis for the perfect lattice yields approximate power-law range dependences which are insensitive to the phonon dispersion law. It is found that the energy-transfer probability range dependences are approximately R^{-6} for electric-dipole and R^{-10} for electric-quadrupole transitions of the impurity ions; these are also the range dependences for Dexter's electric dipole-

dipole and electric quadrupole-quadrupole mechanisms, respectively.

It is shown that the virtual-phonon mechanism is most important in a lattice of light, closely spaced, and highly charged ions and when the energy transferred is small. The virtual-phonon transfer rates can be of the same order as the electronic multipole-multipole rates, for reasonable values of lattice ion charge, mass and spacing, when the energy transferred is sufficiently small. It is also shown that the presence of local modes can increase the virtual-phonon transfer rate for the odd case by orders of magnitude. Therefore, in cases where local modes are present, the virtual-phonon mechanism could strongly dominate the electric dipole-dipole mechanism.

It should be pointed out that the virtual-phonon mechanism will occur concurrently with the Dexter mechanisms, since the same electronic matrix elements are involved. What we have shown is that under certain conditions the phonon mediated interaction can be predominant.

APPENDIX A: CALCULATION OF $\mathcal{H}_{o,e}'^{(2)}$

First consider the case where the excited and ground electronic states of an impurity have opposite parity (odd case). Then $\langle p | r^2 Z_{20} | p' \rangle = 0$ and only the term involving rZ_{10} contributes. Taking the zero-order states of the electron-phonon system to be

$$|p, p'; n_1, n_2, \dots, n_N\rangle = \Psi_p(\mathbf{r}_1) \Psi_{p'}(\mathbf{r}_2) |n_1, n_2, \dots, n_N\rangle, \quad (\text{A1})$$

then the following matrix elements of V_1' [Eq. (9)] exist:

$$\begin{aligned} \langle p', p'; n_1, n_2, \dots, n_q \pm 1, \dots, n_N | V_1' | p, p'; n_1, n_2, \dots, n_q, \dots, n_N \rangle \\ = \frac{8\alpha_{10}}{a^3} \left(\frac{\hbar}{2MN\omega_q} \right)^{1/2} \left\{ \frac{(n_q+1)^{1/2} e^{ik_q da}}{(n_q)^{1/2} e^{-ik_q da}} \right\} \langle p' | r_1 Z_{10}(\theta_1, \varphi_1) | p \rangle \sum_{j=1}^{\infty} \frac{(-1)^j}{j^3} \sin^2(\tfrac{1}{2} k_j a). \end{aligned} \quad (\text{A2})$$

The matrix elements for V_2' are obtained from (A2) by substituting $\langle p | r_2 Y_{10}(\theta_2, \varphi_2) | p' \rangle$ for $\langle p' | r_1 Y_{10}(\theta_1, \varphi_1) | 0 \rangle$ and $-da$ for $+da$. Also, $\langle n_q \pm 1 | V_1' | n_q \rangle = \langle n_q | V_1' | n_q \pm 1 \rangle^*$. $\mathcal{H}_{o,e}'^{(2)}$ is then given by

$$\begin{aligned} \mathcal{H}_{o,e}'^{(2)} \equiv \sum_m \frac{V_{lm} V_{mn}}{E_{mn}} = \sum_k \left\{ \frac{\langle p', p'; n_k | V_1' | p, p'; n_k + 1 \rangle \langle p, p'; n_k + 1 | V_2' | p, p'; n_k \rangle}{\Delta_{pp'} - \hbar\omega_k} \right. \\ + \frac{\langle p', p'; n_k | V_1' | p, p'; n_k - 1 \rangle \langle p, p'; n_k - 1 | V_2' | p, p'; n_k \rangle}{\Delta_{pp'} + \hbar\omega_k} \\ + \frac{\langle p', p'; n_k | V_2' | p', p'; n_k + 1 \rangle \langle p', p'; n_k + 1 | V_1' | p, p'; n_k \rangle}{-\Delta_{pp'} - \hbar\omega_k} \\ \left. + \frac{\langle p', p'; n_k | V_2' | p', p'; n_k - 1 \rangle \langle p', p'; n_k - 1 | V_1' | p, p'; n_k \rangle}{-\Delta_{pp'} + \hbar\omega_k} \right\}, \quad (\text{A3}) \end{aligned}$$

where the sum is over the N points in the first Brillouin zone and $\Delta_{pp'}$ is the energy difference between the excited and ground states of the impurity ion. Using (A2) and the equivalent results for V_2' in (A3) gives

$$\begin{aligned} \mathcal{H}_{o,e}'^{(2)} = \frac{32\alpha_{10}^2 \hbar}{MN a^6} |\langle p | r Y_{10} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^3} \sum_k \frac{1}{\omega_k} \left\{ \frac{e^{-ikR}(n_k+1)}{\Delta_{pp'} - \hbar\omega_j} + \frac{e^{ikR}n_k}{\Delta_{pp'} + \hbar\omega_k} + \frac{e^{ikR}(n_k+1)}{-\Delta_{pp'} - \hbar\omega_k} + \frac{e^{-ikR}n_k}{-\Delta_{pp'} + \hbar\omega_k} \right\} \\ \times \sin^2(\tfrac{1}{2} k_j a) \sin^2(\tfrac{1}{2} k_{j'} a) \end{aligned}$$

or

$$\mathcal{H}_0'^{(2)} = \frac{64\alpha_{10}^2\hbar}{MNa^6} |\langle p | r Y_{10} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^3} \sum_k \frac{1}{\omega_k} \left\{ \frac{\hbar\omega_k \cos(kR) - \Delta \sin(kR)}{\Delta_{pp'}^2 - (\hbar\omega_k)^2} \right\} \sin^2(\frac{1}{2}kja) \sin^2(\frac{1}{2}kj'a), \quad (\text{A4})$$

where $R=2da$, the distance between the impurities. Taking $\omega_k=\omega_{-k}$, and since k ranges between the symmetric limits $\pm\pi/a$, the term involving $\sin(kR)$ in (A4) sums to zero and

$$\mathcal{H}_0'^{(2)} = \frac{64\alpha_{10}^2\hbar^2}{MNa^6} |\langle p | r Y_{10} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^3} \sum_k \frac{\cos kR \sin^2(\frac{1}{2}kja) \sin^2(\frac{1}{2}kj'a)}{\Delta_{pp'}^2 - (\hbar\omega_k)^2}. \quad (\text{A5})$$

If the parities of the excited and ground states of the impurity are the same (even case) then only the term involving r^2Z_{20} in V_i' contributes. Computation of $\mathcal{H}_e'^{(2)}$ is carried out as for $\mathcal{H}_0'^{(2)}$ with the result

$$\mathcal{H}_e'^{(2)} = \frac{36\alpha_{20}^2\hbar^2}{MNa^8} |\langle p | r^2 Y_{20} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^4} \sum_k \frac{\cos kR \sin kja \sin kj'a}{\Delta_{pp'}^2 - (\hbar\omega_k)^2}. \quad (\text{A6})$$

APPENDIX B: CALCULATION OF $\mathcal{H}_{o,e}''^{(2)}$

For the odd case, the matrix elements of V_i'' [Eq. (10)] are the following:

$$\begin{aligned} \langle p', p'; n_k \pm 1, n_{k'} \pm 1 | V_1'' | p, p'; n_k, n_{k'} \rangle = & -\frac{i12\alpha_{10}\hbar \langle p' | r_1 Y_{10}(\theta_1, \varphi_1) | p \rangle}{MNa^4(\omega_k\omega_{k'})^{1/2}} \sum_i \frac{(-i)^j}{j^4} \sin(kja) \sin^2(\frac{1}{2}k'ja) \\ & \times \left\{ \begin{array}{l} -(n_k+1)^{1/2} e^{ikda} \\ (n_k)^{1/2} e^{-ikda} \end{array} \right\} \left\{ \begin{array}{l} (n_{k'}+1)^{1/2} e^{ik'da} \\ (n_{k'})^{1/2} e^{-ik'da} \end{array} \right\}, \quad (\text{B1}) \end{aligned}$$

where the upper quantities in the curly brackets correspond to the addition of phonons and lower quantities correspond to subtraction of phonons from the lattice. The matrix elements of V_2'' are obtained from (B1) by substituting $\langle p | r_2 Z_{10}(\theta_2, \varphi_2) | p' \rangle$ for $\langle p' | r_1 Z_{10}(\theta_1, \varphi_1) | p \rangle$ and $-da$ for $+da$. $\mathcal{H}_o''^{(2)}$ is then given by

$$\begin{aligned} \mathcal{H}_o''^{(2)} = \sum_{k_1 k'} \left\{ \frac{\langle p', p'; n_k, n_{k'} | V_1'' | p, p'; n_k \pm 1, n_{k'} \pm 1 \rangle \langle p, p'; n_k \pm 1, n_{k'} \pm 1 | V_2'' | p, p'; n_k, n_{k'} \rangle}{\Delta_{pp'} - \hbar(\pm\omega_k \pm \omega_{k'})} \right. \\ \left. + \frac{\langle p', p'; n_k, n_{k'} | V_2'' | p', p'; n_k \pm 1, n_{k'} \pm 1 \rangle \langle p', p'; n_k \pm 1, n_{k'} \pm 1 | V_1'' | p, p'; n_k, n_{k'} \rangle}{-\Delta_{pp'} - \hbar(\pm\omega_k \pm \omega_{k'})} \right\}. \quad (\text{B2}) \end{aligned}$$

Using (B1) and equivalent expressions for V_2'' in (B2) gives

$$\begin{aligned} \mathcal{H}_o''^{(2)} = & \left(\frac{12\alpha_{10}\hbar}{a^4 M N} \right)^2 |\langle p | r Y_{10} | p' \rangle|^2 \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^4} \\ & \times \sum_{k,k'} \left\{ \frac{(n_k+1)(n_{k'}+1)e^{i(k+k')R}}{\Delta_{pp'} - \hbar(\omega_k + \omega_{k'})} + \frac{n_k n_{k'} e^{-i(k+k')R}}{\Delta_{pp'} + \hbar(\omega_k + \omega_{k'})} + \frac{(n_{k+1})n_{k'} e^{i(k-k')R}}{\Delta_{pp'} - \hbar(\omega_k - \omega_{k'})} + \frac{n_k(n_{k'+1})e^{-i(k-k')R}}{\Delta_{pp'} + \hbar(\omega_k - \omega_{k'})} \right. \\ & \left. + \frac{(n_{k+1})(n_{k'+1})e^{-i(k+k')R}}{-\Delta_{pp'} - \hbar(\omega_k + \omega_{k'})} + \frac{n_k n_{k'} e^{i(k+k')R}}{-\Delta_{pp'} + \hbar(\omega_k + \omega_{k'})} + \frac{(n_{k+1})n_{k'} e^{-i(k-k')R}}{-\Delta_{pp'} - \hbar(\omega_k - \omega_{k'})} + \frac{n_k(n_{k'+1})e^{i(k-k')R}}{-\Delta_{pp'} + \hbar(\omega_k - \omega_{k'})} \right\} \\ & \times \frac{1}{\omega_k \omega_{k'}} \sin^2(kja) \sin^4(\frac{1}{2}k'ja) \sin^2(kj'a) \sin^4(\frac{1}{2}kj'a), \quad (\text{B3}) \end{aligned}$$

where $R=2da$. The curly bracket reduces to

$$\left\{ \right\} = 2 \left\{ \frac{(n_k + n_{k'} + 1)}{\Delta_{pp'}^2 - \hbar^2(\omega_k + \omega_{k'})^2} [\hbar(\omega_k + \omega_{k'}) \cos(k+k')R - i\Delta_{pp'} \sin(k+k')R] \right. \\ \left. + \frac{(n_k + n_{k'})}{\Delta_{pp'}^2 - \hbar^2(\omega_k - \omega_{k'})^2} [\hbar(\omega_k - \omega_{k'}) \cos(k-k')R - i\Delta_{pp'} \sin(k-k')R] \right\}. \quad (\text{B4})$$

Taking $\Delta_{pp'} \gg \hbar\omega_c$, $\hbar^2(\omega_k \pm \omega_{k'})$ may be neglected in the denominators of (B4). Using this result in (B3) gives, on dropping the terms involving $\sin(k \pm k')R$,

$$\mathcal{H}_e''^{(2)} = \frac{9\alpha_{10}^2(4\hbar)^3 |\langle p | r Y_{10} | p' \rangle|^2}{(a^4 M N \Delta_{pp'})^2} \sum_{j,j'=1}^{\infty} \frac{(-1)^{j+j'}}{(jj')^4} \sum_{k,k'} \left[\frac{(n_{k'} + \frac{1}{2})}{\omega_{k'}} + \frac{(n_k + \frac{1}{2})}{\omega_k} \right] \\ \times \cos(kR) \cos(k'R) \sin(kja) \sin^2(\frac{1}{2}k'ja) \sin(kj'a) \sin^2(\frac{1}{2}k'j'a). \quad (\text{B5})$$

$\mathcal{H}_e''^{(2)}$ is obtained in a similar way and is given in Eq. (21) in the main text.

Phonon Optical Properties of $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2^{\dagger\dagger}$

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The phonon optical properties of the mixed fluorite system $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ are treated theoretically using the "average-Green's-function" formalism. The calculations are based on a rigid-ion model for the pure CaF_2 lattice, with a defect model for Sr^{++} impurities that includes both mass and force-constant changes. Results are compared with experimental observations on Raman scattering and far-infrared reflectivity spectra.

I. INTRODUCTION

THE general problem of the effects of impurities on the vibrational, electronic, and magnetic properties of crystalline solids has currently attracted much interest. One aspect of this problem has been the study of random disordered systems, and in recent years, there have been numerous experimental and theoretical investigations of the phonon optical properties of mixed crystal systems. We have studied experimentally¹ the Raman scattering (at ~ 4 , 77, and 300°K) from the mixed fluorite systems $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ and $\text{Ba}_{1-x}\text{Sr}_x\text{F}_2$ using laser excitation and a photon-counting detection system. Analogous work on the far-infrared reflectivity spectra for these systems has been carried out by Verleur and Barker.² In this paper we shall present a detailed discussion of the numerical methods used, and the results obtained, in an analysis of this experiment. A partial account of some of these results has appeared previously.³

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[‡] Based on part of the Ph.D. thesis of W. B. Lacina, Harvard University, 1969 [Technical Report No. ARPA-36 (unpublished)].

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² H. W. Verleur and A. S. Barker, Jr., Phys. Rev. **164**, 1169 (1967); Solid State Commun. **5**, 695 (1967).

³ P. S. Pershan and W. B. Lacina, in *Light Scattering Spectra of Solids*, edited by G. B. Wright (Springer-Verlag, New York, 1969), p. 439.

The Green's-function methods which have been extensively employed for the isolated defect and random disorder problems are briefly reviewed in Sec. III, where it will be shown how the phonon optical properties can be expressed using this formalism. These techniques have been very useful for qualitative and quantitative understanding of impurity effects, although they usually involve cumbersome computational difficulties for physically realistic models of the impurity and the host lattice. A low concentration theory for Raman scattering and infrared absorption in mixed crystals, based on an average Green's function (\mathbf{G}), is described and applied to the $\text{Ca}_{1-x}\text{Sr}_x\text{F}_2$ system in Sec. IV; theoretical calculations are presented and compared with experimental measurements. The "proper self-energy" (PSE) functions which arise in this formalism are calculated to first order in the concentration x , and involve certain unperturbed phonon Green's functions $G_{\alpha\beta}^0(lk, l'k'; \omega + i\epsilon)$ which have been computed numerically for CaF_2 , using a rigid-ion model of a harmonic fluorite lattice. Some of these Green's functions, as well as some of the details concerning their computation, have been included in the Appendix, since it is likely that they would be useful for many other studies of phonon impurity problems involving CaF_2 . For example they could also be applied to problems of defect-induced Raman scattering or infrared absorption from U centers, to vibrational sidebands in electronic fluorescence spectra, to neutron scattering, etc.

The literature in this field has been expanding so rapidly that it would be futile to attempt to cite all of the work that has been done. An excellent and extremely