Phonon-Induced Ion-Ion Coupling in Paramagnetic Salts*

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The zero-point phonon vibrations in a paramagnetic crystal are shown to give rise to an effective ion-ion coupling. Expressions are derived for ion-energy transitions Δ both greater and less than the phonon-cutoff energy $\hbar\omega_0$. In the former case, the coupling is short range, falling off as $(\hbar\omega_0/2\Delta)^{2[(r_{jj'}/a)-2]}$, where $r_{jj'}$ is the ion-ion separation distance and a the lattice constant. In the latter case, a slowly decreasing oscillatory range dependence is obtained. When the ionic separation is greater than the phonon wavelength appropriate to the transition energy Δ (i.e., when $\lambda > h\nu_s/\Delta$, where ν_s is the sound velocity), the coupling due to transverse phonons falls off very slowly, $\sim(\Delta/\hbar\nu_t)^2[\cos(r_{jj'}\Delta/\hbar\nu_t)]/r_{jj'}$, where ν_t is the transverse sound velocity, a result similar to that of McMahon and Silsbee. Finally, in the limit of vanishing Δ, our results go over smoothly to a range dependence similar to that found by Sugihara, and Aminov and Kochelaev, $\sim 1/R^3$. Numerical estimates are made for the strength of the coupling coefficient.

I. INTRODUCTION

IT was Sugihara[1] who first proposed that two spatially separated paramagnetic ions could be coupled together by the virtual emission of a phonon at one site and its subsequent reabsorption at another site. Sugihara's treatment made no allowance for a change in energy of the paramagnetic ion during this phonon-exchange process. Allowance for an energy change, termed "retardation," was included in a calculation by Aminov and Kochelaev,[2] though only in a qualitative manner. A subsequent paper by McMahon and Silsbee[3] examined these terms in more detail, but did not separate out the contributions from transverse and longitudinal phonons.

In this paper we shall examine the effects of retardation on phonon-induced ion–ion coupling for two quite different limits. In the first case, we shall consider the "extreme" retardation limit where the paramagnetic ion's change in energy Δ exceeds the band pass or maximum phonon frequency $\hbar\omega_0$. This limit, which has apparently not been investigated, is important for energy transfer in solids, though it will turn out that the interaction will be one of very short range. In the other limit, when Δ is less than the maximum phonon energy, we find a long-range oscillatory interaction similar to that found in Refs. 2 and 3. This latter result reduces smoothly to that found by Sugihara[1] in the limit that $\Delta \to 0$.

For both limits, we treat only the coupling between identical ions, involving identical energy changes on either ion. If the ion pair's total energy is not conserved in the interaction process (i.e., if the reduction in energy Δ at one ion is not exactly compensated by a corresponding increase in energy of Δ at the other ion), then the emitted (absorbed) phonon must differ in energy from the absorbed (emitted) phonon in order to compensate for this energy mismatch. It is not difficult to show that interference terms reduce the probability of this process to zero. Only emission and absorption of identical phonons can lead to a nonvanishing ion–ion interaction. The case of lack-of-energy conservation in ion–ion interactions is treated by Dexter[4] and in a recent paper by one of us[5] (R.O.). In that paper, there is also given a brief summary of the results to be derived here in the limit of extreme retardation.

In Sec. II we formulate the ion–ion interaction process via virtual phonon emission and absorption. Section III treats the extreme retardation limit $\Delta > \hbar\omega_0$ and Sec. IV the weak (or in-band) retardation region, $\Delta < \hbar\omega_0$. Section V concludes with a numerical estimate for the effectiveness of this coupling mechanism, and a discussion of some examples where it is expected to be important.

II. ION-ION COUPLING—FORMULATION

The origin of the proposed ion–ion coupling lies in the creation (destruction) of a phonon at the site of one paramagnetic ion and the destruction (creation) of the same phonon at the site of another ion. This "phonon exchange" is very similar to the well-known example of "photon exchange" which leads to the usual Coulombic interaction between charged particles.[6] We begin with an expression for the one-phonon orbit-lattice interaction appropriate to a paramagnetic ion at the center of the jth octahedron of ligand charges:

$$\mathcal{H}_j = \sum_{l=2,4,6} \sum_{m=\theta,e} V(\Gamma_{3g} l) C(\Gamma_{3g} l, m)_j Q(\Gamma_{3g}, m)_j + \sum_{l=2,4,6} \sum_{m=0,\pm 1} V(\Gamma_{5g} l) C(\Gamma_{5g} l, m)_j Q(\Gamma_{5g}, -m)_j (-1)^m. \quad (1)$$

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Here, $V(\Gamma_{ig}, l)$ is an interaction constant with units of energy, appropriate to the ith irreducible representation of the octahedral group. The $C(\Gamma_{ig}l, m)$ and $Q(\Gamma_{ig}, m)_j$ are, respectively, linear combinations of Racah's $C_{lm}=\sum_n[4\pi/(2l+1)]^{1/2}Y_l^m(n)$ and the normal modes of vibration (divided by a, the lattice constant), transforming as the mth subvector of the Γ_{ig} irreducible representation of the octahedral group. The $C(\Gamma_{ig}l, m)_j$ are given in a number of papers[7] and will not be reproduced here. The $Q(\Gamma_{ig}, m)_j$ are listed below for later use. For simplicity of notation, we write

$$Q(\Gamma_{ig}, m)_j=\sum_{\mathbf{k},s}(i/a)[\hbar/2M\omega(\mathbf{k}, s)]^{1/2}[b_{\mathbf{k},s}e^{i\mathbf{k}\cdot\mathbf{r}_j}-b_{\mathbf{k},s}^{+}e^{-i\mathbf{k}\cdot\mathbf{r}_j}]R_{\mathbf{k},s}(\Gamma_{ig}, m), \tag{2}$$

where the sum is over all wave vectors and polarization indices $\mathbf{k}$ and s, respectively. In Eq. (2), M is the mass of the crystal, $\hbar\omega(\mathbf{k}, s)$ the energy of the phonon with wave vector $\mathbf{k}$ and polarization index s, $b_{\mathbf{k},s}$ the destruction operator for the same phonon, and $R_{\mathbf{k},s}(\Gamma_{ig}, m)$ is given below for the various terms appropriate to an octahedral ligand environment:

$$\begin{aligned}
R_{\mathbf{k},s}(\Gamma_{3g}, \theta) &= \tfrac{1}{2}[2e^z(\mathbf{k}, s)\ \sin k_z a-e^x(\mathbf{k}, s)\ \sin k_x a-e^y(\mathbf{k}, s)\ \sin k_y a],\\
R_{\mathbf{k},s}(\Gamma_{3g}, e) &= \tfrac{1}{2}\sqrt{3}[e^x(\mathbf{k}, s)\ \sin k_x a-e^y(\mathbf{k}, s)\ \sin k_y a],\\
R_{\mathbf{k},s}(\Gamma_{5g}, 1) &= -i[\sqrt{(3/2)}][e^y(\mathbf{k}, s)\ \sin k_z a+e^z(\mathbf{k}, s)\ \sin k_y a+ie^z(\mathbf{k}, s)\ \sin k_x a+ie^x(\mathbf{k}, s)\ \sin k_z a],\\
R_{\mathbf{k},s}(\Gamma_{5g}, 0) &= i\sqrt{3}[e^x(\mathbf{k}, s)\ \sin k_y a+e^y(\mathbf{k}, s)\ \sin k_x a],\\
R_{\mathbf{k},s}(\Gamma_{5g}, -1) &= i[\sqrt{(3/2)}][e^y(\mathbf{k}, s)\ \sin k_z a+e^z(\mathbf{k}, s)\ \sin k_y a-ie^z(\mathbf{k}, s)\ \sin k_x a-ie^x(\mathbf{k}, s)\ \sin k_z a],
\end{aligned} \tag{3}$$

where $e^\alpha(\mathbf{k}, s)$ is the αth component of the (unit) polarization vector for the phonon of wave vector $\mathbf{k}$ and polarization index s. The expressions given in (2) and (3) are very similar to those of Van Vleck[8] and, in the long-wavelength limit, $k_\alpha a\ll 1$, reduce to those given by Schawlow *et al.*[9] and independently by Blume and Orbach.[7]

We write the single-ion orbit-lattice coupling in the manner of (1) in order to separate out phonon from spin contributions. This separation is, in general, *not* valid if retardation effects are significant, i.e., if a change in electronic energy Δ occurs at a given ion "during" the phonon-exchange process. Then, the ion–ion coupling constants will be shown to be functions of the change in ionic energy.

To be more specific, we consider the effective Hamiltonian constructed from the use of (1) in second order at ion sites j and j'. Because retardation is important, we specify that the ions at $\mathbf{r}_j$ and $\mathbf{r}_{j'}$ are initially in the states $|j^*\rangle$ and $|j'\rangle$, respectively. "After" the process of phonon exchange, the ions are found to be in states $|j\rangle$ and $|j'^*\rangle$, respectively. We assume the energy difference between $|j^*\rangle$ and $|j\rangle$ equals that between $|j'^*\rangle$ and $|j'\rangle$, and we denote it by Δ. The effective ion–ion coupling Hamiltonian for an exchange of phonons of energy $\hbar\omega$ is then of the form

$$\begin{aligned}
\mathcal{H}_{\text{eff}} = &\frac{\langle j, j'^*|\,\mathcal{H}_{j'}\,|j, j'\rangle\langle j, j'|\,\mathcal{H}_j\,|j^*, j'\rangle}{\Delta\mp\hbar\omega}\\
&+\frac{\langle j, j'^*|\,\mathcal{H}_j\,|j^*, j'^*\rangle\langle j^*, j'^*|\,\mathcal{H}_{j'}\,|j^*, j'\rangle}{-\Delta\mp\hbar\omega}.
\end{aligned} \tag{4}$$

Here, $|j, j'^*\rangle$ represents the product spin states $|j\rangle|j'^*\rangle$, and the $\mp\hbar\omega$ appearing in the denominator depend on whether phonon emission or absorption is occurring in the first matrix element of each term. The next step is to sum (4) over all phonons of wave vector $\mathbf{k}$ and polarization index s. For the *particular* mth subvector of the ith irreducible representation in (1), this leads to

$$\begin{aligned}
\mathcal{H}_{\text{eff}}^{i,m} = &\sum_{l,l'}V_j(\Gamma_{ig}l)\,V_{j'}(\Gamma_{ig}l')\\
&\times\langle j, j'^*|\,C_{j'}(\Gamma_{ig}, -m)\,|j, j'\rangle\\
&\times\langle j, j'|\,C_j(\Gamma_{ig}, m)\,|j^*, j'\rangle\\
&\times\sum_{\mathbf{k},s}\left\{\frac{\hbar}{2M\omega(\mathbf{k}, s)a^2}\,\frac{2\hbar\omega(\mathbf{k}, s)}{\Delta^2-[\hbar\omega(\mathbf{k}, s)]^2}\right.\\
&\left.\times\cos(\mathbf{k}\cdot\mathbf{r}_{jj'})R_{\mathbf{k},s}(\Gamma_{ig}, m)R_{\mathbf{k},s}(\Gamma_{ig}, -m)\right\},
\end{aligned} \tag{5}$$

where $\mathbf{r}_{jj'}=\mathbf{r}_j-\mathbf{r}_{j'}$. Expression (5) serves as the starting point of our investigation into the phonon-induced ion–ion coupling. Note that all reference to the phonon-occupation numbers has canceled out of (5), leaving only the effect of zero-point vibrations. This is an exact result, true in the presence of retardation, as well as in its absence. It remains, now, to evaluate the sum over phonon coordinates $\mathbf{k}$ and s for the two extremes discussed in the Introduction.

III. EXTREME RETARDATION, $\Delta\gg\hbar\omega_0$

In this section, we evaluate (5) for ion-transition energies Δ greater than the maximum phonon energy

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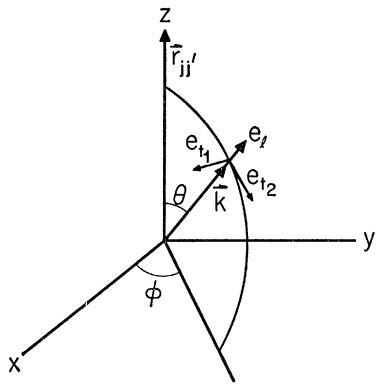

FIG. 1. The coordinate system used for the calculation of the phonon-induced ion-ion interaction. The z direction is taken parallel to the line joining the two ions, and e_l, e_{t_1}, e_{t_2} label the directions of polarization of the longitudinal and transverse branches, respectively.

$\hbar\omega_0$. To accomplish this, it is necessary to assume a specific form for the phonon-dispersion law $\omega(\mathbf{k}, s)$. For simplicity we choose the form

$$\omega^2=\omega_{0s}^2\,[\sin^2\tfrac{1}{2}(k_xa)+\sin^2\tfrac{1}{2}(k_ya)+\sin^2\tfrac{1}{2}(k_za)], \quad (6)$$

where the subscript s labels the longitudinal and transverse branches. This result is appropriate for a simple cubic lattice with nearest-neighbor coupling only. The reason for the necessity of specifying a dispersion law comes from the singular character of the denominator in (5) when $\hbar\omega=\Delta$. Using (6) (and *not* a Debye approximation) we see this occurs for complex $\mathbf{k}$. Hence, from (5), the interaction will be short range and, as we shall show, falls off as $\exp\{(-2r_{jj'}/a)\ \ln(2\Delta/\hbar\omega_0)\}$. This result might have been anticipated since the coupling requires that a frequency $\omega=\Delta/\hbar$ be transmitted by a lattice which cuts off its propagating wave character at $\omega=\omega_0\ll\Delta/\hbar$. To be explicit, consider the case of $i=3$, $m=e$. The curly bracket in (5) becomes

$$\frac{-3\hbar^2}{4Ma^2}\sum_{\mathbf{k},s}\frac{[e^x(\mathbf{k}, s)\ \sin k_xa-e^y(\mathbf{k}, s)\ \sin k_ya]^2}{\Delta^2-[\hbar\omega(\mathbf{k}, s)]^2}\cos\mathbf{k}\cdot\mathbf{r}_{jj'}. \quad (7)$$

For simplicity we shall choose the k_z direction parallel to the line connecting the two ions $\mathbf{r}_{jj'}$. The simplest way we have found to evaluate (7) is to expand the denominator in powers of $[\hbar\omega(\mathbf{k}, s)]^2/\Delta^2$ and then to evaluate the resulting expression term by term. For longitudinal phonons, (7) becomes

$$\frac{-3\hbar^2}{4Ma^2\Delta^2}\sum_n\left[\left(\frac{\hbar\omega_{0l}}{\Delta}\right)^{2n}\sum_k\frac{1}{k^2}\,(k_x\sin k_xa-k_y\sin k_ya)^2\right.$$
$$\left.\times[(\sin^2\tfrac{1}{2}k_xa)+(\sin^2\tfrac{1}{2}k_ya)+(\sin^2\tfrac{1}{2}k_za)]^n\cos(k_zr_{jj'})\right]. \quad (8)$$

This expression can be integrated in a straightforward, if tedious, manner. Two types of terms obtain, according to whether $r_{jj'}$ differs from or equals na. In the former case, for $r_{jj'}/a\gg1$, the above expression integrates to (longitudinal phonons)

$$-\frac{9\hbar^2}{4\pi\rho\Delta^2}\left[\frac{1}{r_{jj'}^5}+O\left(\frac{a^2}{r_{jj'}^7}\right)\right]. \quad (9a)$$

In the latter case, when $r_{jj'}=na$, special attention must be given to the last term in the second square brackets of (8). To the lowest order in $\hbar\omega_{0l}/\Delta$, this part of (8) becomes (longitudinal phonons)

$$-\frac{3\hbar^2}{4Ma^2\Delta^2}\sum_n\left\{\left(\frac{\hbar\omega_{0l}}{\Delta}\right)^{2n}\sum_k\frac{1}{k^2}\,[k_x\sin k_xa-k_y\sin k_ya]^2\right.$$
$$\left.\times\left[\frac{(-1)^n}{2^{2n}}\{\cos[(na-r_{jj'})k_z]+\cos[(na+r_{jj'})k_z]\}\right]\right\}=-\frac{3\hbar^2\gamma_l}{4\rho a^5\Delta^5}\,(-1)^{r_{jj'}/a}\left(\frac{\hbar\omega_{0l}}{2\Delta}\right)^{2r_{jj'}/a}, \quad (9b)$$

where it is understood that $r_{jj'}>0$ in the last line and

$$\gamma_l=(1/N)\sum_k(1/k^2)[k_x\sin k_xa-k_y\sin k_ya]^2.$$

For transverse phonons we adopt the coordinate system shown in Fig. 1. In a manner identical to the derivation of (9a) and (9b), and in the limit that $r_{jj'}/a\gg1$, (7) reduces to

$$\{\sum_{i=1,2}(-3\hbar^2\gamma_{t_i}/4\rho a^5\Delta^2)\,(-1)^{r_{jj'}/a}(\hbar\omega_{0t_i}/2\Delta)^{2r_{jj'}/a}\}-(9\hbar^2/4\pi\rho\Delta^2)[-(1/r_{jj'}^5)+O(a^2/r_{jj'}^7)], \quad (10)$$

where

$$\gamma_{t_i}=N^{-1}\sum_k[e^x(\mathbf{k}, t_i)\ \sin k_xa-e^y(\mathbf{k}, t_i)\ \sin k_ya]^2.$$

This is a remarkable result for it shows that to this order in $(\hbar\omega_{0s}/\Delta)$ the power-law terms in $(1/r_{jj'})$ exactly cancel when the contributions from the longitudinal (9a) and two transverse (10) phonons are added. The cancellation of these terms is model-independent since it arises from the neglect of $\hbar\omega$ as compared to Δ in the denominator of (7). There are terms of higher order in $(\hbar\omega_{0s}/\Delta)$ in (7), entering as $(1/r_{jj'})^9(\hbar\omega_{0s}/\Delta)^2$, but these can be shown to exactly cancel if $\omega_{0l}=\omega_{0t}$. In general this is not the case. However, as we shall show in Sec. V, the magnitude of the phonon-induced spin–spin coupling coefficients at near-neighbor distances are of the order of the electric quadrupole-quadrupole interaction which falls off as $(1/r_{jj'})^5$. Hence these higher-order terms which survive the cancellation occurring between (9a) and (10) are

negligible in practice and will not be considered further here. Finally, then, all that remains of (7) is simply

$$\sum_s (3\hbar^2\gamma_s/4\rho a^5\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0s}/2\Delta)^{2r_{ij'}/a}, \quad (11)$$

where

$$\gamma_s=(1/N)\sum_{\mathbf{k}}[e^x(\mathbf{k},s)\ \sin k_x a-e^y(\mathbf{k},s)\ \sin k_y a]^2.$$

This result can easily be rewritten in the exponential form mentioned earlier in the first part of this section. One may evaluate the other terms summed in the curly bracket of (5) in a similar manner. In each case, the lowest-order power-law terms cancel when the contributions of transverse and longitudinal phonons are added. The results are listed below for each value of i and m, including the above result (11) for completeness:

$i=3, \quad m=0$

l: $(-\hbar^2/4\rho a^5\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0l}/2\Delta)^{[2(r_{ij'}/a)-4]}$;

t_1: 0;

t_2: $(-\hbar^2/2\rho a^5\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t}/2\Delta)^{[2(r_{ij'}/a)-4]}$; (12a)

$i=3, \quad m=e$

l: $(3\hbar^2\gamma_l/4\rho a^5\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0l}/2\Delta)^{2r_{ij'}/a}$;

t_1: $(3\hbar^2\gamma_{t_1}/4\rho a^5\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t_1}/2\Delta)^{2r_{ij'}/a}$;

t_2: $(3\hbar^2\gamma_{t_2}/4\rho a^5\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t_2}/2\Delta)^{2r_{ij'}/a}$; (12b)

where

$$\gamma_s=N^{-1}\sum_{\mathbf{k}}[e^x(\mathbf{k},s)\ \sin k_x a-e^y(\mathbf{k},s)\ \sin k_y a]^2;$$

$i=5, \quad m=0$

l: $(3\hbar^2\gamma_l'/\rho a^2\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0l}/2\Delta)^{2r_{ij'}/a}$;

t_1: $(3\hbar^2\gamma_{t_1}'/\rho a^2\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t_1}/2\Delta)^{2r_{ij'}/a}$;

t_2: $(3\hbar^2\gamma_{t_2}'/\rho a^2\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t_2}/2\Delta)^{2r_{ij'}/a}$; (13a)

where

$$\gamma_s'=N^{-1}\sum_{\mathbf{k}}[e^x(\mathbf{k},s)\ \sin k_y a+e^y(\mathbf{k},s)\ \sin k_x a]^2;$$

and

$i=5, \quad m=\pm 1$

l: $(-3\hbar^2/8\rho a^2\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0l}/2\Delta)^{[2(r_{ij'}/a)-4]}$;

t_1: $(-3\hbar^2/16\rho a^2\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t_1}/2\Delta)^{[2(r_{ij'}/a)-4]}$;

t_2: $(-3\hbar^2/16\rho a^2\Delta^2)(-1)^{r_{ij'}/a}(\hbar\omega_{0t_2}/2\Delta)^{[2(r_{ij'}/a)-4]}$. (13b)

It should be noted that (12a) and (13b) have considerably longer ranges than (12b) or (13a), though of course even these fall off rapidly for very large $r_{jj'}/a$. At nearer distances, however, for the case of strong orbit-lattice coupling, it may well be the case that (12a) and (13b), corresponding to $i=3$, $m=0$ and $i=5$, $m=\pm 1$ type terms, are important. Numerical estimates for the strength of this part of the ion–ion interaction are given in Sec. V.

IV. "IN-BAND" LIMIT, $\Delta<\hbar\omega_0$

We evaluate (5) in this section for ion-transition energies Δ less than the maximum phonon energy $\hbar\omega_0$. The principal contributions to $\mathcal{H}_{\text{eff}}^{i,m}$ will come from phonons of energy $\hbar\omega\sim\Delta$, as can be seen from the form of (5). If we assume the phonon-frequency surfaces are smoothly varying in the vicinity of this energy, it turns out that the coupling Hamiltonian will be relatively insensitive to the periodic character of the frequency–wave-vector dependence. This was not the case for the extreme retardation limit because of the need for complex $\mathbf{k}$ necessary for equality of $\hbar\omega$ and Δ. The lack of need for an explicitly periodic form for $\omega(\mathbf{k}, s)$ simplifies the computation of the "in-band" terms greatly. We shall assume in what follows a linear dependence of $\omega(k, s)$ on k. The quantitative error introduced by this assumption will not be great for Δ significantly less than $\hbar\omega_0$ and will enable us to display some very interesting physical consequences of the in-band phonon-induced ion–ion coupling. We take

$$\omega(\mathbf{k},s)=v_s k \quad (14)$$

and define a "resonance" wave vector $k_\Delta{}^s$ for each phonon branch by

$$k_\Delta{}^s=\Delta/\hbar v_s. \quad (15)$$

We shall drop the superscript s in what follows for convenience, reinserting the mode label only in our final results. Using (14) and (15), Eq. (5) reduces to

$$\sum_s \frac{1}{Ma^2 v_s{}^2}\sum_{\mathbf{k}}\frac{\cos(\mathbf{k}\cdot\mathbf{r}_{jj'})}{k^2-k_\Delta{}^2} \times R_{\mathbf{k},s}(\Gamma_{ig},m)R_{\mathbf{k},s}(\Gamma_{ig}-m). \quad (16)$$

Consistent with the assumption (14), we shall, in what follows, adopt the long-wavelength form for the $R_{\mathbf{k},s}(\Gamma_{ig}, m)$, defined in (3). It is, in fact, possible to solve (16) exactly without this assumption, but identical results are obtained when the long-wavelength approximation is made in the final result. We shall evaluate (16) for the interesting case of $i=3$, $m=0$ explicitly below. Our results will differ from those of Sugihara in the limit $\Delta\to 0$ for this case, though an identical result to his will obtain for the case of $m=e$. Because of our differing conclusions regarding $m=0$, we go through the calculation in some detail here. We must evaluate, taking $k_z \parallel \mathbf{r}_{jj'}$,

$$\frac{1}{4}\sum_{\mathbf{k}}\frac{\cos(k_z r_{jj'})(2e^z k_z a-e^x k_x a-e^y k_y a)^2}{k^2-k_\Delta{}^2}. \quad (17)$$

For longitudinal phonons this reduces to

$$\frac{a^2}{4}\sum_{\mathbf{k}}\frac{\cos(k_z r_{jj'})(2k_z{}^2-k_x{}^2-k_y{}^2)^2}{k^2(k^2-k_\Delta{}^2)}. \quad (18)$$

This sum can be converted into an integral and, assuming $r_{jj'}\gg a$, is easily evaluated using polar coordinates. Inserting the result into (16), we find (16) to be

equal to

$i=3,\ m=0$ (longitudinal phonons)

$$\frac{1}{4\pi\rho v_l^2}\left\{\frac{k_\Delta^2}{r_{jj'}}\cos(k_\Delta r_{jj'})-\frac{6k_\Delta\sin(k_\Delta r_{jj'})}{(r_{jj'})^2}-\frac{24}{(r_{jj'})^3}\cos(k_\Delta r_{jj'})+\frac{54}{k_\Delta(r_{jj'})^4}\sin(k_\Delta r_{jj'})-\frac{54}{k_\Delta^2(r_{jj'})^5}[1-\cos(k_\Delta r_{jj'})]\right\}. \quad (19)$$

This is an interesting result in that, for $r_{jj'}>1/k_\Delta\sim\lambda_\Delta$, the phonon wavelength corresponding to the ion-transition energy Δ, the ion–ion interaction falls off very slowly as $\cos(k_\Delta r_{jj'})/r_{jj'}$. This results in an extremely long-range coupling. Though we shall show the coefficient to be rather small, the extreme range of the interaction may make it significant in many practical cases. In the opposite limit, $r_{jj'}\ll 1/k_\Delta$, which corresponds to that of zero retardation, (19) reduces to

$$3/4\pi\rho v_l^2(r_{jj'})^3. \quad (20)$$

This result should be compared with that of Sugihara[1] which predicted a $(1/r_{jj'})^5$ behavior for the $i=3$, $m=0$ term. We see that this is not the case, and we shall show that the characteristic $(1/r_{jj'})^3$ behavior obtains for all i and m in the limit that $r_{jj'}<1/k_\Delta$. A similar conclusion was also reached by Aminor and Kochelaev[2] in the zero-retardation limit.

For transverse phonons we again adopt the coordinate system shown in Fig. 1. In this case, (17) is found to vanish for the polarization t_1, and, for t_2 to equal,

$i=3,\ m=0$ (transverse phonons)

$$\frac{9}{8\pi\rho v_t^2}\left\{\frac{k_\Delta\sin(k_\Delta r_{jj'})}{(r_{jj'})^2}+\frac{5\cos(k_\Delta r_{jj'})}{(r_{jj'})^3}-\frac{12\sin(k_\Delta r_{jj'})}{k_\Delta(r_{jj'})^4}+\frac{12}{k_\Delta^2(r_{jj'})^5}[1-\cos(k_\Delta r_{jj'})]\right\}. \quad (21)$$

Again, a slower fall-off than $(r_{jj'})^{-3}$ is obtained when $r_{jj'}>1/k_\Delta\sim\lambda_\Delta$. It is interesting to note that *if* we set $v_t=v_l$ (as done by Sugihara[1] and Aminov and Kochalaev[2]) and add (21) to (19), the last two terms in both expressions cancel and we are left with

$$(v_t=v_l=v)$$

$$\frac{1}{8\pi\rho v^2}\left[\frac{2k_\Delta^2\cos(k_\Delta r_{jj'})}{r_{jj'}}-\frac{3k_\Delta\sin(k_\Delta r_{jj'})}{(r_{jj'})^2}-\frac{3\cos(k_\Delta r_{jj'})}{(r_{jj'})^3}\right]. \quad (22)$$

This result is identical with that of McMahon and Silsbee.[3] Again, in the zero-retardation limit, where $r_{jj'}\ll 1/k_\Delta$, Eq. (21) reduces to

$$-[3/8\pi\rho v^2(r_{jj'})^3], \quad (23)$$

which again displays the characteristic $(1/r_{jj'})^3$ dependence of the phonon-induced ion–ion coupling.

In general, $v_t\neq v_l$ and we should expect that (21) will dominate (19) since $v_t<v_l$. In addition, the fact that $k_\Delta{}^t>k_\Delta{}^l$ also enhances the importance of the transverse contribution over the longitudinal at long distances.

It is a straightforward, but very tedious, matter to compute the magnitude of (16) for the four other values of i and m. For simplicity we define

$$F_1^{(s)}=[(k_\Delta^{(s)})^2\cos(k_\Delta^{(s)}r_{jj'})/r_{jj'}];$$
$$F_2^{(s)}=[k_\Delta^{(s)}\sin(k_\Delta^{(s)}r_{jj'})/(r_{jj'})^2];$$
$$F_3^{(s)}=[\cos(k_\Delta^{(s)}r_{jj'})/(r_{jj'})^3];$$
$$F_4^{(s)}=[\sin(k_\Delta^{(s)}r_{jj'})/k_\Delta^{(s)}(r_{jj'})^4];$$
$$F_5^{(s)}=\{[1-\cos(k_\Delta^{(s)}r_{jj'})]/(k_\Delta^{(s)})^2(r_{jj'})^5\}. \quad (24)$$

Then, using the coordinate system shown in Fig. 1, we obtain the following values for the integral (16):

$i=3,\ m=0$

l: $(1/4\pi\rho v_l^2)[F_1^{(l)}-6F_2^{(l)}-24F_3^{(l)}+54F_4^{(l)}-54F_5^{(l)}]$;
t_1: 0;
t_2: $(9/8\pi\rho v_t^2)[F_2^{(t)}+5F_3^{(t)}-12F_4^{(t)}+12F_5^{(t)}]$;

$i=3,\ m=e$

l: $(3/4\pi\rho v_l^2)[-F_3^{(l)}+3F_4^{(l)}-3F_5^{(l)}]$;
t_1: $(3/16\pi\rho v_t^2)[F_2^{(t)}+F_3^{(t)}]$;
t_2: $(3/16\pi\rho v_t^2)[F_2^{(t)}+5F_3^{(t)}-12F_4^{(t)}+12F_5^{(t)}]$;

$i=5,\ m=0$

l: $(3/\pi\rho v^2)[F_3^{(l)}-3F_4^{(l)}+3F_5^{(l)}]$;
t_1: $(3/4\pi\rho v_t^2)[F_2^{(t)}+F_3^{(t)}]$;
t_2: $(-3/4\pi\rho v_t^2)[F_2^{(t)}+5F_3^{(t)}-12F_t^{(4)}+12F_t^{(5)}]$;

$i=5,\ m=\pm 1$

l: $(3/\pi\rho v_l^2)[F_2^{(l)}+5F_3^{(l)}-12F_4^{(l)}+12F_5^{(l)}]$;
t_1: $(3/8\pi\rho v_t^2)[F_1^{(t)}-2F_2^{(t)}-2F_3^{(t)}]$;
t_2: $(3/8\pi\rho v_t^2)[F_1^{(t)}-8F_2^{(t)}-40F_3^{(t)}+96_4F^{(t)}-96F_5^{(t)}]$. (25)

We have repeated our previous results for $i=3$, $m=0$ in Eq. (25) for completeness. If we take $v_l=v_t$ and add our results for each of the individual values of i and m, our expressions reduce to those of McMahon and Silsbee.[3] We believe that the different coupling and range behavior displayed in (25) for longitudinal and transverse phonons warrants the presentation of these results. Nevertheless, it is true that the physical properties predicted by McMahon and Silsbee[3] for phonon-induced spin–spin coupling are reproduced here.

A few remarks can be made concerning the relative importance of the terms in (25) before numerical estimates are given. First, in the limit that $r_{jj'}\ll 1/k_\Delta{}^{(s)}$ (zero retardation) all of the individual terms in (25) fall off as $(1/r_{jj'})^3$, and with coefficients in agreement with those given by Aminov and Kochelaev.[2] Next, in the limit that $r_{jj'}>1/k_\Delta{}^{(s)}$ (first achieved for the transverse-phonon branches, t_1 and t_2) the $i=5$, $m=\pm 1$ terms give the longest-range interaction, falling off only as $(k_\Delta{}^{(t)})^2\cos(k_\Delta{}^{(t)}r_{jj'})/r_{jj'}$. Similarly, the longitudinal-phonon contribution for $i=3$, $m=0$ also falls off in this manner, though the requirement that $k_\Delta{}^{(t)}>k_\Delta{}^{(l)}$ reduces its magnitude compared to the transverse $i=5$, $m=\pm 1$ term. Finally, the results presented in (25) do not take into account finite-phonon lifetimes. It is clear that at sufficiently long range ($r_{jj'}\sim v_s\tau_s$, where τ_s is the lifetime of the $k_\Delta{}^{(s)}$ phonon) this damping will convert the oscillatory character of (25) into an exponentially damped result. Explicit results are difficult to obtain, however, because of the need for consideration of the detailed phonon-decay mechanism. In general, it is *not* correct to simply insert an imaginary wave vector in the denominator of (16), as demonstrated for the Ruderman–Kittel interaction by de Gennes.[10] One can certainly use (25) with safety, however, in the limit that $|\mathbf{r}_{jj'}|<v_s\tau_s$.

V. NUMERICAL ESTIMATES FOR $\mathcal{H}_{\rm eff}{}^{i,m}$

The importance of $\mathcal{H}_{\rm eff}{}^{i,m}$ will depend greatly on the particular system under investigation. The range of significant interaction for $\mathcal{H}_{\rm eff}{}^{i,m}$, in the limit of extreme retardation, will clearly depend on the ratio of the ion-transition energy Δ to the maximum phonon energy $\hbar\omega_0$. The coefficients of the powers of $(\hbar\omega_{0l}/2\Delta)$ appearing in this limit, as given by (5), (12), and (13), are of the form

$$V^2\hbar^2/\rho a^5\Delta^2, \tag{26}$$

where V^2 represents the factors contained in the first four terms of (5), and is related to the square of the strength of the crystalline electric field. Thus, for iron group ($3d$) ions, V may be of the order of 10^4 cm^{-1}, whereas for rare earths it will be more like $\sim$100 cm^{-1}. In both cases, the coupling introduced by $\mathcal{H}_{\rm eff}{}^{i,m}$ may be responsible for energy transfer between ions spatially separated from one another. It has been shown by Dexter,[4] Axe *et al.*,[11] Brown *et al.*,[12] and Imbusch[13] that quadrupole–quadrupole coupling may be the dominant mechanism for energy transfer in a number of hosts. This coupling is of the form

$$\mathcal{H}_{\rm QQ}=\frac{4\pi e^2\langle r_j{}^2\rangle\langle r_{j'}{}^2\rangle}{5\epsilon_{jj'}r_{jj'}{}^5}\sum_{-2}^{+2}c_mY_{2m}(j)\,Y_{2-m}(j'), \tag{27}$$

where $c_m=c_{-m}$, $c_0=6$, $c_1=-4$, and $c_2=1$. The quantity $\epsilon_{jj'}$ represents the dielectric constant appropriate to the separation $\mathbf{r}_{jj'}$ and $\langle r_j{}^2\rangle$ is the mean-square radius of the magnetic electron. It is interesting to compare (26) and (27) for some specific cases. In ruby, for example, Imbusch[13] has examined in detail the R_1 energy-transfer process. Very roughly, $2\Delta\sim 28\hbar\omega_0$ for Al_2O_3:Cr^{3+}. This implies a very short range of interaction, even for a large coefficient (26). Inserting values for the coefficients appearing in (12) and (27) appropriate to ruby, we find for the representative term $i=5$, $m=\pm 1$

$$\mathcal{H}_{\rm eff}{}^{5,\pm 1}/\mathcal{H}_{\rm QQ}$$

$$\cong(0.1)\,(r_{jj'}/a)^5(-1)^{[(r_{ij'}/a)-1]}(\hbar\omega_0/2\Delta)^{2[(r_{ij'}/a)-2]}. \tag{28}$$

Thus, though the coefficient (26) is only a tenth of the strength of the quadrupole–quadrupole coupling, the two powers of $(2\Delta/\hbar\omega_0)$ appearing in (28) at near-neighbor distances cause the phonon-induced coupling to dominate the electrostatic coupling. When $r_{jj'}>2a$, $\mathcal{H}_{\rm eff}{}^{i,m}$ rapidly diminishes in importance.

For rare-earth ions, Δ may be somewhat smaller than in the iron group series. However, the coupling coefficients are undoubtedly considerably weaker so that $\mathcal{H}_{\rm eff}{}^{i,m}$ in the extreme retardation limit will probably only be important for those cases where Δ lies slightly above and close to $\hbar\omega_0$.

The in-band case is one where not only the electric-quadrupole interaction but also the magnetic-dipole coupling can seriously compete with $\mathcal{H}_{\rm eff}{}^{i,m}$. It has been demonstrated by McMahon and Silsbee[3] that for $\Delta\sim 0$ the latter mechanism is comparable to $\mathcal{H}_{\rm eff}{}^{i,m}$. As Δ increases, it is clear from (25) that the phonon-induced coupling becomes larger in range, falling off only as $1/r_{jj'}$ when $r_{jj'}$ exceeds $1/k_\Delta{}^{(s)}$. Hence, for greater distances, $\mathcal{H}_{\rm eff}{}^{i,m}$ will dominate the dipolar coupling. At present, we are unable to find a specific material which exhibits this effect. We feel that the explicit form given in (25) for this coupling may assist in its identification.

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