pling is independent of temperature. Also shown is the normalized field at the Cl sites. Since the field at the Cl ion is primarily due to type-A chains, the Néel temperature is taken as 4.84 °K. Normalized to this temperature, the field and thus the magnetization, as measured by the Cl NMR, have the same temperature dependence as $H^{\perp}_{\text{int}}$ and $H^{\parallel}_{\text{int}}$ at the Cs site. These three magnetization curves also agree with the reduced neutron diffraction magnetization curve.[4] The reduced magnetization obtained from the Brillouin function for $S=1$ is represented by the solid line in Fig. 9. Figure 10 shows a graph of $H^{\parallel}_{\text{int}}$ and $H^{\perp}_{\text{int}}$ vs $(1-T/T_N)$, which gives the critical exponent β as 0.32 ± 0.03 for both $m^{\perp}$ and $m^{\parallel}$.

The Cl NMR in $RbNiCl_3$ gave essentially the same results, except that the magnitude of $\vec{H}_{\text{int}}$ was different. Work is underway on the Rb NMR investigation in the $RbNiCl_3$.

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Interference and Intermediate-Level-Width Corrections to the Orbach Relaxation Rate*

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A modification of the Orbach relaxation process arising from the phonon-induced intermediate level width is developed. It is shown from a numerical integration, including all two-phonon terms (resonant, interference, nonresonant), that the temperature dependence of the two-phonon spin-lattice relaxation process at temperatures intermediate between the Orbach and Raman regimes can be substantially altered. Thus, determination of excited-state splittings using the temperature dependence of the Orbach relaxation rate can be misleading, should experimental considerations limit the range over which T measurements are made. In general, the effect of the intermediate level width is to diminish the slope of $1/T_1$ vs $1/T$, yielding an apparent reduction in the excited splitting as compared to optical determinations. An apparent concentration dependence of the exponent in the Orbach relaxation process can also obtain from the same source, by virtue of a change in the sound velocity changing the intermediate level width.

I. INTRODUCTION

A well-known spin-lattice relaxation process in both iron-group and rare-earth paramagnetic salts was first proposed by Finn, Orbach, and Wolf[1] in terms of a two-step direct process. Later, Orbach,[2] and independently Aminov,[3] recast the process in terms of a two-phonon process analogous to resonance fluorescence in gases. These two approaches each have their appropriate regime, having to do with the origin of the linewidth of the intermediate level. In all treatments to date, the two-phonon contribution to the relaxation rate has been divided into two parts: resonant

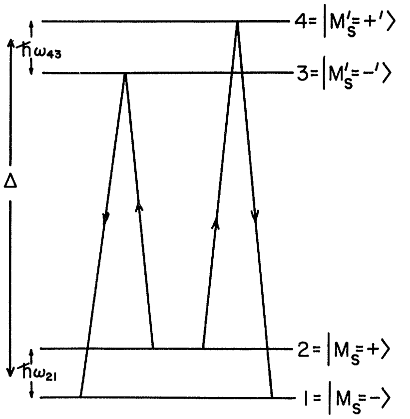

FIG. 1. Schematic energy levels: The labels 1, 2 (3, 4) indicate the ground (excited) states split by Zeeman energy $\hbar\omega_{21}(\hbar\omega_{43})$. The arrows show the transitions via two-phonon process.

and Raman. The linewidth of the intermediate level has been regarded as infinitesimally narrow for the resonant contribution.

The purpose of this paper is to first point out that a finite intermediate level width, together with other terms in the relaxation rate integrand, can change the temperature dependence of the relaxation rate appreciably. We shall estimate the character (i.e., effect on the temperature dependence of the spin-lattice relaxation time) of these effects and their magnitude. For example, we shall show that the exponential temperature slope of the relaxation rate is altered in the low-temperature regime where Raman and Orbach processes are of comparable magnitude. Further, a concentration dependence (because of sound-velocity changes) can also obtain even for relatively narrow excited-state widths. This last observation is relevant to the experiments of Young and Stapleton,[4] who exhibited a concentration-dependent relaxation activation energy, and fitted their results assuming a broad inhomogeneous intermediate level width (using a Gaussian distribution). The exponential temperature dependence would favor the low-energy "wing" of the broadened excited state, so that an apparent decrease of slope of $1/T_1$ with $1/T$ is obtained in their model as the broadening increases. Our approach also will yield a decrease of slope, but it relies on the phonon (homogeneous) broadening of the intermediate level. This has some formal similarity to Young and Stapleton, but utilizes a Lorentzian distribution and has nothing to do with crystalline defects, etc.

In Sec. II we shall develop the theory, and in Sec. III we shall apply our results to the La$(\mathrm{Cl}_{1-x}\mathrm{Br}_x)_3$: Er system investigated by Young and Stapleton.[4]

II. FORMULATION OF THEORY

We shall not rederive the entire two-phonon spin-lattice relaxation expression. Partial presentations can be found in the original papers of Orbach[2] and Aminov,[3] with improved formalisms in the work of Orbach and Tachiki,[5] and finally Orbach and Stapleton.[6] The results of these approaches can be summarized in the following (complete) expression for the two-phonon relaxation rate. [The expression (1) contains the peculiar off-diagonal terms first found by Culvahouse and Richards,[7] (CR) who used a density-matrix method. The equivalence of these two approaches is proved in the Appendix. Also, see Fig. 1 for a pictorial view of the transitions leading to (1).] We get

$$\frac{1}{T_{10}}=\frac{4\pi}{\hbar^2}\sum_{\vec{k},s,\vec{k}',s'}\Bigg|\sum_{i,l,m,i',l',m'}V(\Gamma_{ig}l)\,V(\Gamma_{i'g}l')(-1)^m(-1)^{m'}\frac{\hbar}{2Ma^2\,\omega(\vec{k},s)^{1/2}\,\omega(\vec{k}',s')^{1/2}}\,[R_{\vec{k},s}(\Gamma_{ig},m)\,R_{\vec{k}',s'}(\Gamma_{i'g},m')$$

$$+(-1)^{2M_s}R_{\vec{k}',s'}(\Gamma_{ig},m)\,R_{\vec{k},s}(\Gamma_{i'g},m')]\,\langle -|\,C(\Gamma_{i'g}l',m')\,|+'\rangle\langle +'|\,C(\Gamma_{ig}l,m)\,|+\rangle$$

$$\times\frac{n_{\vec{k},s}{}^{1/2}(n_{\vec{k}',s'}+1)^{1/2}}{\Delta-\hbar\omega(\vec{k},s)-i(\Gamma_{+'}/2)}+(-1)^{2M_s}\frac{n_{\vec{k},s}{}^{1/2}(n_{\vec{k}'s'}+1)^{1/2}}{\Delta+\hbar\omega(\vec{k}',s')}\Bigg|^2\,\delta[\omega(\vec{k}),s)-\omega(\vec{k}',s')]\,, \quad (1)$$

where Δ, $\omega(k,s)$, $n_{\vec{k},s}$, a, M, and $\Gamma_{+'}$ are, respectively, the energy separation of the excited level, the frequency appropriate to the phonon with wave vector $\vec{k}$ and polarization s, the occupation number of that mode, the lattice constant, the mass of the whole crystal, and finally the phonon-induced width of the excited level. Zeeman energies $\hbar\omega_{21}$, $\hbar\omega_{43}$ are neglected in the energy denominators. For Kramers (non-Kramers) transitions $2M_s$ is even (odd). $C(\Gamma_{ig}l)$ and $R_{\vec{k},s}(\Gamma_{ig},m)$ are, respectively, linear combinations of the Racah normalized spherical harmonics, and certain functions of $\vec{k}$ for a given polarization index s, transforming as the mth subvector of the Γ_{ig} irreducible representation describing the vibrations of the ligand complexes surrounding the paramegnetic ion. They are listed in detail in Ref. 6. Finally, $V(\Gamma_{ig},l)$ are interaction constants with units of energy, appropriate to the lth spherical harmonic component of the ith representation.

In a long-wavelength limit $R_{\vec{k},s}(\Gamma_{ig}, m)$ is proportional to the wave number so that we can set $R_{\vec{k},s}(\Gamma_{ig}, m) \equiv k\tilde{R}_{\hat{k},s}(\Gamma_{ig}, m)$, where $\tilde{R}_{\hat{k},s}(\Gamma_{ig}, m)$ depends only on the direction $\hat{k}$ of $\vec{k}(\hat{k}=\vec{k}/|\vec{k}|)$ and the polarization index s. Using the Debye approximation for the density of phonon states, the relaxation rate (1) can be simplified to (ρ_0 is the mass density of the crystal)

$$\frac{1}{T_{10}} = \frac{4\pi}{(2\rho_0 a^2)(2\pi)^6} \sum_{s,s'} \frac{1}{v_s^5 v_{s'}^5} \int d\Omega_{\hat{k}} \int d\Omega_{\hat{k}'} \left| \sum_{i,l,m,i',l',m'} V(\Gamma_{ig} l) V(\Gamma_{i'g} l')(-1)^m (-1)^{m'} [R_{\hat{k},s}(\Gamma_{ig}, m)\tilde{R}_{\hat{k}',s'}(\Gamma_{i'g}, m') + (-1)^{2M_s} \tilde{R}_{\hat{k}',s'}(\Gamma_{ig}, m)\tilde{R}_{\hat{k},s}(\Gamma_{i'g}, m')] \langle - | C(\Gamma_{i'g} l' m') | +' \rangle \langle +' | C(\Gamma_{ig} l, m) | + \rangle \right|^2 \int_0 d\omega_{\vec{k},s} \times \omega_{\vec{k},s}^6 n(\omega_{\vec{k},s})[n(\omega_{\vec{k},s})+1] \left\{ \frac{1}{[\Delta - \hbar\omega(\vec{k},s)]^2 + (\Gamma_{+'}/2)^2} + \frac{1}{[\Delta + \hbar\omega(\vec{k},s)]^2} + \frac{(-1)^{2M_s} 2[\Delta - \hbar\omega(\vec{k},s)]}{[(\Delta - \hbar\omega(\vec{k},s))^2 + (\Gamma_{+'}/2)^2][\Delta + \hbar\omega(\vec{k},s)]} \right\}, \quad (2)$$

where $\Omega_{\hat{k}}$ is a solid angle in $\vec{k}$ space.

If we neglect the last two terms in the last curly bracket, and approximate the first (Lorentzian-like) term as $(2\pi/\Gamma_{+'})\delta[\Delta - \hbar\omega(\vec{k},s)]$, in the limit that $\Gamma_{+'} \to 0$, we obtain the full Culvahouse-Richards[7] expression for the Orbach relaxation rate at low temperatures [this result is independent of the Debye or long-wavelength approximation (see the Appendix)]:

$$\frac{1}{T_{10}} = \frac{4B_1B_2}{(B_1+B_2)} \left(1 + (-1)^{2M_s} \frac{|C|^2}{B_1B_2}\right) n(\Delta), \quad (3)$$

where $n(\Delta) = (e^{\Delta/kT} - 1)^{-1}$, and the matrix elements B_1, B_2, and C are defined explicitly in the Appendix.

The functional dependence of (3) on the excited-energy splitting at low temperatures (i.e., $1/T_{10} \sim e^{-\Delta/kT}$) can be used to determine Δ from spin-lattice-relaxation measurements. However, as pointed out by Young and Stapleton, there appears to be a systematic discrepancy between the value of Δ so determined, and that found from direct optical-absorption measurements[8]: the former is always smaller than the latter. In fact, the apparent decrease of slope of (3) from that expected from optical measurements has a natural explanation, arising essentially from the resonant term in (2) which was approximated as a δ function in the limit of the excited-level width $\Gamma_{+'} \to 0$. Practically, $\Gamma_{+'}$ is not that small. One finds values of $\Gamma_{+'}/2\Delta \approx 10^{-2} - 10^{-3}$ characteristic of a number of systems. These values are sufficient to decrease the slope of $1/T_{10}$-vs-$1/T$ curve appreciably even in the "pure" exponential regime, for a few decades in $1/T_{10}$.

Additional contributions arise from the remainder of the terms in the last large parentheses which were dropped in the process of obtaining (3). Numerical calculations discussed below will demonstrate that the contribution from these terms is of the same order of magnitude as that from the first, or the resonant term, when the temperature is such that the Raman and the resonant (Orbach) rates are comparable. This will further tend to decrease the slope of the curve near the tail of the Orbach regime. Thus, we are suggesting an additional (perhaps complementary) explanation for the discrepancy between the relaxation and optical values for Δ, to that of Young and Stapleton.

The relaxation rate (2) can be rewritten in a more compact form within the long-wavelength and Debye approximation (see the Appendix), by extending the upper limit of the integral to infinity, appropriate to the low-temperature regime ($\Theta_D/T \gg 1$):

$$\frac{1}{T_{10}} = B\int_0^\infty dx \frac{x^6 e^{-x\Delta/kT}}{(1-e^{-x\Delta/kT})^2} \left(\frac{1}{(1-x)^2+\gamma^2} + \frac{1}{(1+x)^2} + (-1)^{2M_s} \frac{2(1-x)}{[(1-x)^2+\gamma^2](1+x)}\right), \quad (4)$$

with

$$B = \frac{2B_1B_2\hbar}{\Delta\pi}\left(1 + (-1)^{2M_s}\frac{|C|^2}{B_1B_2}\right) \quad \text{and} \quad \gamma = \frac{\Gamma_{+'}}{2\Delta}.$$

The function preceding the large parentheses in the integrand of (4) is sharply peaked at $x = 6kT/\Delta$. Thus, for very low temperatures ($kT \ll \Delta/6$), most of the contribution of the integral comes from a small region near $x = 0$. The function in the large parentheses can then be expanded in a Taylor series about $x = 0$, and one finds a leading term proportional to T^9 and T^7, respectively, for Kramers and non-Kramers transitions, independent of γ for $\gamma \ll 1$. These are the usual Raman relaxation rates. In this temperature region the contribution from the Lorentzian peak at $x = 1$ is completely quenched by

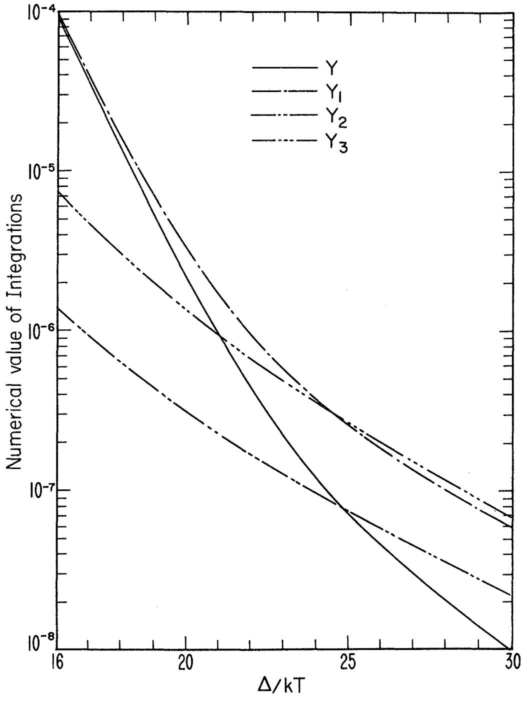

FIG. 2. Plot of the numerical integration of (4) for Kramers ion for $\gamma = 0.0041$, showing the magnitude of the contribution from the terms Y_i defined by $1/T_{10} \equiv BY \equiv B(Y_1 + Y_2 - Y_3)$.

the sharply decaying tail of the exponential for practical values of γ (of the order of 10^{-3}). For substantially larger temperatures ($kT \sim \Delta/6$) the Lorentzian peak will be dominant, and we will obtain a pure Orbach relaxation expression [identical to (2)], with $1/T_{10} \sim e^{-\Delta/kT}$, without regard to the value of γ, as long as $\gamma \ll 1$.

For temperatures intermediate to these two extremes (we shall show in Sec. III that most experiments of $1/T_{10}$ include this region) numerical evaluation of (4) is necessary. Close to the "pure" Orbach regime of this temperature range the resonant term is dominant. The expression for this term can be interpreted as an average of the Orbach process with respect to the "variable energy separation" of the excited level over a Lorentzian distribution function centered at Δ with a width $\Gamma_{+'} = 2\gamma\Delta$. Because of the slowly decreasing nature of Lorentzian function, even a small γ ($\sim 10^{-2}$–10^{-3}) can appreciably decrease the slope of the curve (by 10–20%). In the middle of this intermediate region, where the Orbach and Raman rates are comparable, all terms in the large parentheses contribute significantly. Figure 2 exhibits the results of a number of numerical integrations of (4), displaying the relative importance of the various terms in the last large parentheses. It is seen that the relaxation rate actually exhibits a T^{10} (Kramers) or T^8 (non-Kramer) dependence over more than a decade before entering the Raman regime. At this point, it should be mentioned that, limited for Raman process, a similar effect, i.e., a T^{10}, $T^{10.5}$, T^{11} dependence has been found by Kiel and Mins,[9] respectively, for Yb, Nd, and Ce in $CaWO_4$. This "anomalous" temperature dependence showing a deviation from "T^9 law" is calculated by numerically integrating the relaxation integral allowing for a finite value of Δ and phonon dispersion, which can lead to a more rapid rise of the Raman term with increasing temperature. The latter fact can also be seen from the derivation of (4). If we include the phonon dispersion, the right-hand side of (4) should be modified by a temperature-dependent factor ζ^{10} arising from the velocity factor $1/v^{10}$ in (2). It will vary from $\zeta = 1$ in pure Orbach regime smoothly to $\zeta = \Delta/\hbar v_s k_\Delta$ $[\omega(k_\Delta) \equiv \Delta/\hbar]$ in pure Raman regime. However, the dispersion may not be too important if the first excited level lies much below the Debye temperature as in our case.

In conclusion, determinations of Δ by "fitting" to a simple exponential plus Raman process can be very misleading, and in fact *always yields a value smaller than* the actual value of Δ, as determined by optical-absorption or emission techniques. Though the cases treated in Fig. 2 are far from exhaustive, they do illustrate the importance of dealing with all the two-phonon terms in the relaxation integrand. It is straightforward, when analyzing a particular experiment, to evaluate (4) using the appropriate parameters so that our treatment is quite general.

In actual practice, evaluation of (4) requires knowledge of γ, the reduced intermediate-state phonon-broadened linewidth. This quantity is not, however, a free parameter, for it is related to the coefficient of the exponential factor in (3). A self-consistency in fitting will be required in any analysis of experimental results. First, a fit to (3) will establish an estimate of the coefficient of the exponential. This number can then be used for a first approximation to γ, and (4) can be evaluated. A few iterations should then suffice to determine γ uniquely. In Sec. III we follow such a procedure for some of the materials investigated by Young and Stapleton.

III. APPLICATION TO EXPERIMENT

In Fig. 3 we compare the theoretical value of the spin-lattice relaxation rate $1/T_1 = 1/T_{10} + AT$ for 1*d*% Er^{170} in La(0.97 Cl, 0.03 Br)$_3$ and La(0.94 Cl, 0.06 Br)$_3$ with the experimental data obtained by Young and Stapleton.[4(b)] We have used their values of A for the direct process, and B and γ are so chosen as to best fit the data in Orbach regime using (4). The parameters are listed in Table I. The agreement is quite good within the

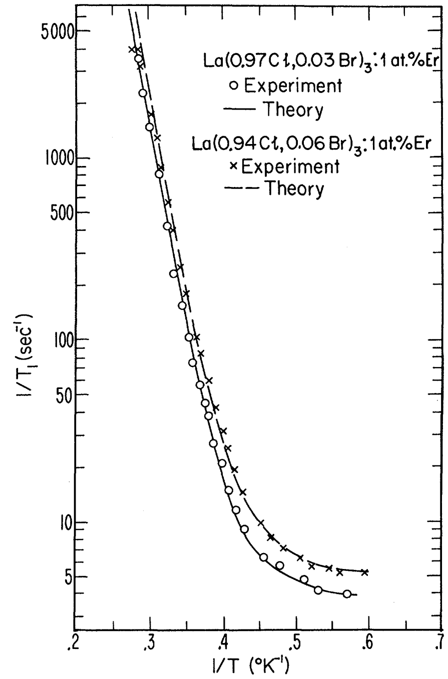

FIG. 3. Comparison of the theory to the experimental data for the temperature dependence of the relaxation rate for 1 at.% Er^{170} in La(0.97 Cl, 0.03 Br)$_3$ and La(0.94 Cl, 0.06 Br)$_3$ at 9.25 GHz taken from Ref. 4(b). The parameters are listed in Table I.

limit of experimental error. The different behavior between the 3-at.% and 6-at.% concentrations is attributed in our model solely to the change in sound velocity. That is, because $A \alpha v^{-5}$, we can use the quoted change in the direct-process rate to scale $B(\alpha v^{-10})$ and $\gamma\,(\alpha v^{-5})$. Thus, in principle (Debye approximation), no free parameters are used in obtaining the 6-at.%-Br curve from the 3-at.%-Br curve. As noted in Sec. II, the effect of the finite value for γ is a reduction of the slope of the relaxation rate in the early part of the Orbach regime.

Young and Stapleton proposed an alternate explanation, based on a spatial distribution of Δ appropriate to locally strained sites (caused, for example, by the replacement of the Cl by a Br). They adopted a Gaussian distribution for Δ, centered around the mean optical value Δ_{op}, with a standard deviation σ. From the Δ dependence of the original Orbach relaxation rate (3), $1/T_{10} = B'\Delta^3\, e^{-\Delta/kT}$, they obtained a modified Orbach relaxation rate with an effective $\Delta_{eff} = \Delta_{op} + 3\sigma^2/\Delta_{op} - \sigma^2/kT$, always smaller than Δ_{op}. By adjusting parameters, σ, B', as well as the coefficients from Raman and direct process, they could fit their data moderately well. The two approaches differ basically in that the decrease of the slope comes, in our case, through the Lorentzian average with relatively narrow homogeneous phonon-induced width and, in their treatment, through the Gaussian average with a broad inhomogeneous width. It is difficult to argue which interpretation is the more appropriate. There is some evidence for a departure from the simple exponential temperature dependence of the Orbach process even in the absence of Br^- doping. On balance, it seems to us that both explanations may be significant, and could contribute to the observed departure of the relaxation rates from a simple activation result. *Only* with detailed knowledge of the inhomogeneities, and their effect on the excited-state splittings, will one be able to make a definitive separation. Nevertheless, we do argue that insofar as the broadening of the excited level is due to phonon emission, the formula (4) must be utilized. *Then*, an averaging procedure by Young and Stapleton may be in order, but *not* before.

IV. CONCLUSION

In conclusion, we have shown that the full two-phonon integrand, including all terms in (4), can substantially alter the temperature dependence of the two-phonon spin-lattice relaxation rate in the intermediate-temperature region. We have also demonstrated that a finite width of the intermediate level can change the slope of $1/T_{10}$-vs-$1/T$ curve for the resonant process. A limited regime of measurement can result in a value of excited-state energy Δ smaller than the actual value if one fits to only a pure Orbach exponential temperature dependence. The degree of departure depends on the phonon-induced linewidth of the intermediate level, γ, which is itself related to the coefficient of the exponential. A self-consistent fitting procedure is required for an accurate determination of γ.

The spatial inhomogeneity in Δ examined by Young and Stapleton, which leads to a similar reduction in Δ as measured in a relaxation-time experiment, is not ruled out by our conclusions, but must be regarded as a supplementary mechanism which, if necessary, ought to be invoked after the effect of the intermediate-level width has been ac-

TABLE I. Best-fitting parameters to the relaxation rate $1/T_1$ of 1% La$(Cl_{1-x}, Br_x)_3$: Er. The first column gives the Br concentration (x) and the parameter A is the coefficient for direct process (AT) quoted from Ref. 4(b). $\gamma\,(=\Gamma/2\Delta)$ is the reduced intermediate-level width while B is defined in (4). An optically determined value of energy separation $\Delta = 54.5\,°K$ is used.

La$(Cl_{1-x}, Br_x)_3$: 1 at.% Er	A (sec^{-1} °K^{-1})	$\gamma(10^{-3})$	B (10^7 sec^{-1})
$x = 0.03$	2.11 ± 0.05	3.00	1.86
$x = 0.06$	2.88 ± 0.12	4.10	3.60

counted for.

Consideration of the effect we have discussed will be important for the spin-lattice relaxation of various rare-earth paramagnetic salts[4,10–12] where the first excited level lies much below the Debye temperature, in the intermediate- (usually liquid-helium) temperature range where both Orbach and Raman processes can be equally important.

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APPENDIX

In this Appendix we prove the equivalence of (1) to the result [see (A8)] of Culvahouse and Richards[7] (referred to as CR hereafter) for Orbach process. We start with a Zeeman-energy-dependent form[6] of (1):

$$\frac{1}{T_{10}}=\frac{4\pi}{\hbar^2}\sum_{\vec{k},s,\vec{k}'s'} n_{\vec{k},s}(n_{\vec{k}',s'}+1)\bigg|\sum_{i,l,m,i',l',m'} V(\Gamma_{ig}l)\,V(\Gamma_{i'g}l')(-1)^m(-1)^{m'}\,\frac{\hbar}{2Ma^2\omega_{\vec{k},s}{}^{1/2}\omega_{\vec{k}',s'}{}^{1/2}}\langle -|C(\Gamma_{i'g}l',m')|+'\rangle$$

$$\times\langle +'|C(\Gamma_{ig}l,m)|+\rangle\bigg[R_{\vec{k},s}(\Gamma_{ig},m)R_{\vec{k}',s'}(\Gamma_{i'g},m')\left(\frac{1}{\Delta^+-\hbar\omega_{\vec{k},s}-i(\Gamma/2)}+\frac{(-1)^{2M_s}}{\Delta^-+\hbar\omega_{\vec{k}',s'}-i(\Gamma/2)}\right)$$

$$+R_{\vec{k}',s'}(\Gamma_{ig},m)R_{\vec{k},s}(\Gamma_{i'g},m')\left(\frac{1}{\Delta^++\hbar\omega_{\vec{k}',s'}-i(\Gamma/2)}+\frac{(-1)^{2M_s}}{\Delta^--\hbar\omega_{\vec{k},s}-i(\Gamma/2)}\right)\bigg]\bigg|^2\,\delta(\omega_{\vec{k},s}-\omega_{\vec{k}',s'}+\omega_{21})\,, \tag{A1}$$

where $\Delta^\pm=\Delta-\frac{1}{2}\hbar\omega_{21}\pm\frac{1}{2}\hbar\omega_{43}$, and other notations are defined in the text. We have assumed $\Gamma_{+'}=\Gamma_{-'}=\Gamma$. (A1) is a second-order transition rate due to the orbit-lattice interaction given by

$$H^{01}=\sum_{i,l,m,\vec{k},s} V(\Gamma_{ig}l)(-1)^m C(\Gamma_{ig}l,m)\,\frac{1}{a}\left(\frac{\hbar}{2M\omega_{\vec{k},s}}\right)^{1/2}(ia_{\vec{k},s}e^{i\vec{K}\cdot\vec{R}}-ia^\dagger_{\vec{k},s}e^{-\vec{K}\cdot\vec{R}})\,R_{\vec{k},s}(\Gamma_{ig},m)\,, \tag{A2}$$

where $a^\dagger_{\vec{k},s}(a_{\vec{k},s})$, $\vec{R}$ are phonon creation (annihilation) operator and position vector of a lattice site, respectively. For Orbach process we drop the nonresonant terms, obtaining

$$\frac{1}{T_{10}}=\frac{4\pi}{\hbar^2}\sum_{\vec{k},s,\vec{k}',s'} n_{\vec{k},s}(n_{\vec{k}',s}+1)\,\frac{\hbar^2}{4M^2a^4\omega_{\vec{k},s}\omega_{\vec{k}',s'}}\sum_{i,l,m,i',l',m',i'',l'',m'',i''',l''',m'''} V(\Gamma_{ig}l)V(\Gamma_{i'g}l')V(\Gamma_{i''g}l'')^*$$

$$\times V(\Gamma_{i'''g}l''')^*\langle -|C(\Gamma_{i'g}l',m'|+'\rangle\langle +'|C(\Gamma_{ig}l,m)|+\rangle(\langle -|C(\Gamma_{i'''g}l''',m''')|+'\rangle$$

$$\times\langle +'|C(\Gamma_{i''g}l'',m''|+\rangle)^*\bigg\{R_{\vec{k},s}(\Gamma_{ig},m)R_{\vec{k},s'}(\Gamma_{i'g},m')R_{\vec{k},s}(\Gamma_{i''g},m'')^*$$

$$\times R_{\vec{k}',s'}(\Gamma_{i'''g},m''')^*\,\frac{1}{(\Delta^+-\hbar\omega_{\vec{k},s})^2+(\Gamma/2)^2}+R_{\vec{k}',s'}(\Gamma_{ig},m)R_{\vec{k},s}(\Gamma_{i'g},m')R_{\vec{k}',s'}(\Gamma_{i''g},m'')^*\,R_{\vec{k},s}(\Gamma_{i'''g},m''')^*$$

$$\times\frac{1}{(\Delta^--\hbar\omega_{\vec{k},s})^2+(\Gamma/2)^2}+(-1)^{2Ms}\bigg[R_{\vec{k},s}(\Gamma_{ig},m)\,R_{\vec{k}',s'}(\Gamma_{i'g},m')\,R_{\vec{k}',s'}(\Gamma_{i''g},m'')^*\,R_{\vec{k},s}(\Gamma_{i'''g},m''')^*$$

$$\times\frac{1}{\Delta^+-\hbar\omega_{\vec{k},s}-i(\Gamma/2)}\;\frac{1}{\Delta^--\hbar\omega_{\vec{k},s}+i(\Gamma/2)}+R_{\vec{k},s}(\Gamma_{i''g},m'')^*\,R_{\vec{k}',s'}(\Gamma_{i'''g},m''')^*\,R_{\vec{k}',s'}(\Gamma_{ig},m)\,R_{\vec{k},s}(\Gamma_{i'g},m')$$

$$\times\frac{1}{\Delta^+-\hbar\omega_{\vec{k},s}+i(\Gamma/2)}\;\frac{1}{\Delta^--\hbar\omega_{\vec{k},s}-i(\Gamma/2)}\bigg]\bigg\}\delta(\omega_{\vec{k},s}-\omega_{\vec{k}',s'}+\omega_{21})\,.$$

The energy-dependent factors appearing in the square bracket can be rewritten as

$$\frac{1}{\Delta^+-\hbar\omega_{\vec{k},s}\mp i(\Gamma/2)}\,\frac{1}{\Delta^--\hbar\omega_{\vec{k},s}\pm i(\Gamma/2)}=\frac{-\hbar\omega_{43}\mp i\Gamma}{(\hbar\omega_{43})^2+\Gamma^2}\left[P\left(\frac{1}{\Delta^+-\hbar\omega_{\vec{k},s}}-\frac{1}{\Delta^--\hbar\omega_{\vec{k},s}}\right)\pm\pi i[\delta(\Delta^+-\hbar\omega_{\vec{k},s})+\delta(\Delta^--\hbar\omega_{\vec{k},s})]\right],$$

where P indicates the principal part. Since $R_{\vec{k},s}$, $n_{\vec{k},s}$ are slowly varying functions of $\hbar\omega_{\vec{k},s}$ near Δ, we can put $\Delta^+\simeq\Delta^-\simeq\Delta$ and drop ω_{21} from the δ function. Hence, setting $1/(\Delta-\hbar\omega_{\vec{k},s})^2+(\Gamma/2)^2=(2\pi/\Gamma)\,\delta(\Delta-\hbar\omega_{\vec{k},s})$, we obtain

$$\begin{aligned}\frac{1}{T_{10}}=\frac{4\pi}{\hbar^2}\,\frac{2\pi}{\Gamma}\sum_{\vec{k},s,\vec{k}',s'}\frac{\hbar^2}{4M^2a^4}\,\frac{n_{\vec{k},s}}{\omega_{\vec{k},s}}\,\frac{(n_{\vec{k}',s'}+1)}{\omega_{\vec{k}',s'}}&\sum_{i,l,m,i',l',m',i'',l'',m'',i''',l''',m'''}V(\Gamma_{ig}l)\,V(\Gamma_{i'g}l')\,V(\Gamma_{i''g}l'')^*\\ &\times V(\Gamma_{i'''g}l''')^*(-1)^m(-1)^{m'}(-1)^{m''}(-1)^{m'''}\langle -|C(\Gamma_{i'g}l',m')|+'\rangle\langle +'|C(\Gamma_{ig}l,m)|+\rangle\\ &\times(\langle -|C(\Gamma_{i'''g}l''',m''')|+'\rangle\langle +'|C(\Gamma_{i''g}l'',m'')|+\rangle)^*\Big[R_{\vec{k},s}(\Gamma_{ig},m)\,R_{\vec{k}',s'}(\Gamma_{i'g},m')\\ &\times R_{\vec{k},s}(\Gamma_{i''g},m'')^*\,R_{\vec{k}',s'}(\Gamma_{i'''g},m''')^*+R_{\vec{k}',s'}(\Gamma_{ig},m)\,R_{\vec{k},s}(\Gamma_{i'g},m')\,R_{\vec{k}',s'}(\Gamma_{i''g},m'')^*\\ &\times R_{\vec{k},s}(\Gamma_{i'''g},m''')^*+(-1)^{2M_s}\Big(\frac{\Gamma^2-i\hbar\omega_{43}\Gamma}{(\hbar\omega_{43})^2+\Gamma^2}\,R_{\vec{k},s}(\Gamma_{ig},m)\,R_{\vec{k}',s'}(\Gamma_{i'i},m')\\ &\times R_{\vec{k}',s'}(\Gamma_{i''g},m'')^*\,R_{\vec{k},s}(\Gamma_{i'''},m''')^*+\frac{\Gamma^2+i\hbar\omega_{43}\Gamma}{(\hbar\omega_{43})^2+\Gamma^2}\,R_{\vec{k},s}(\Gamma_{i''g},m'')^*\\ &\times R_{\vec{k}',s'}(\Gamma_{i'''g},m''')^*\,R_{\vec{k}',s'}(\Gamma_{ig},m)\,R_{\vec{k},s}(\Gamma_{i'g},m')\Big)\Big]\hbar\,\delta(\Delta-\hbar\omega_{\vec{k},s})\,\delta(\Delta-\hbar\omega_{\vec{k}',s'})\;.\end{aligned}\tag{A3}$$

Neglecting $n(\Delta)$ compared to unity and using the Hermitian property of the operator $\sum_{i,l,m}V(\Gamma_{ig},l)\,R_{\vec{k},s}(\Gamma_{ig},m)\times C(\Gamma_{ig},l,m)$, (A3) can be further simplified as

$$\begin{aligned}\frac{1}{T_{10}}=\frac{4\pi}{\hbar^2}\,\frac{2\pi}{\Gamma}\,\hbar\,n(\Delta)\,\frac{\hbar^2}{4M^2a^4}\Big(2\sum_{\vec{k},s,\vec{k}',s'}\frac{1}{\omega_{\vec{k},s}\,\omega_{\vec{k}',s'}}&\Big|\sum_{i,l,m,i''',l''',m'''}V(\Gamma_{ig}l)\,V(\Gamma_{i'''g}l''')(-1)^m(-1)^{m'''}\\ &\times\langle +'|C(\Gamma_{ig}l,m)|+\rangle\langle +'|C(\Gamma_{i'''g}l''',m''')|-\rangle R_{\vec{k},s}(\Gamma_{ig},m)\,R_{\vec{k}',s'}(\Gamma_{i'''g},m''')\Big|^2\,\delta(\Delta-\hbar\omega_{\vec{k},s})\,\delta(\Delta-\hbar\omega_{\vec{k}',s'})\\ &+(-1)^{2M_s}\,2\,\frac{\Gamma^2}{(\hbar\omega_{43})^2+\Gamma^2}\Big|\sum_{\vec{k},s,i,l,m,i''',l''',m'''}V(\Gamma_{ig},l)\,V(\Gamma_{i'''g},l''')\\ &\times\frac{1}{\omega_{\vec{k},s}}(-1)^m(-1)^{m'''}\langle +'|C(\Gamma_{ig},l,m)|+\rangle\langle +'|C(\Gamma_{i'''g},l''',m''')|-\rangle\,R_{\vec{k},s}(\Gamma_{ig},m)\\ &\times R_{\vec{k},s}(\Gamma_{i'''g},m''')\,\delta(\Delta-\hbar\omega_{\vec{k},s})\Big|^2\Big)\;.\end{aligned}\tag{A4}$$

The phonon-induced width (Γ) of the intermediate level is given by[6]

$$\Gamma'_{+}=\frac{\pi\hbar}{Ma^2}\sum_{\vec{k},s,j=\pm}\Big|\sum_{i,l,m}\frac{1}{\omega_{\vec{k},s}^{1/2}}\,V(\Gamma_{ig},l)\,R_{\vec{k},s}(\Gamma_{ig},m)\,\langle j|C(\Gamma_{ig},l,m)|+'\rangle\,(n_{\vec{k},s}+1)^{1/2}\Big|^2\,\delta(\Delta-\omega_{\vec{k},s})\;.\tag{A5}$$

We designate the spontaneous part of this as

$$\underset{\Gamma+'\to+}{\text{spont}}=\hbar\,B_1,\quad\underset{\Gamma+'\to-}{\text{spont}}=\hbar\,B_2\;.\tag{A6}$$

Substituting (A5) and (A6) into (A4) we can identify the first term (to be defined as I) as

$$\mathrm{I}=[4\,B_1B_2/(B_1+B_2)]\,n(\Delta)\;,$$

which is the first term of. To further identify the second term of (A4) with that of CR's Eq. (48), we change our notation to theirs. Their interaction Hamiltonian is given by

$$H'=\sum_{\lambda,r}V_r^{(\lambda)}Q_r^{(\lambda)}\;,$$

with

$$Q_r^{(\lambda)}=\sum_{\vec{k},s}F_r^{(\lambda)}(\vec{k},s)(a_{\vec{k},s}\,e^{i\vec{k}\cdot\vec{R}}+a^{\dagger}_{\vec{k},s}\,e^{-i\vec{k}\cdot\vec{R}})\;.$$

(For definitions of symbols see Ref. 7.) Therefore we can replace $\sum_{i,l,m}V(\Gamma_{ig},l)R(\Gamma_{ig},m)\,C(\Gamma_{ig},l,m)$ by $\sum_{r,\lambda}a(2M\omega_{\vec{k},s}/\hbar)^{1/2}V_r^{(\lambda)}F_r^{(\lambda)}$ (where $\omega_{\vec{k},s}=\Delta/\hbar$) in the second term (to be defined as II) of (A4). Thus,

$$\mathrm{II}=\frac{4\pi}{\hbar^2}\,\frac{2\pi}{\Gamma}\,\hbar n(\Delta)\frac{\hbar^2}{4M^2a^4}\,(-1)^{2M_s}\frac{\Gamma^2}{(\hbar\omega_{43})^2+\Gamma^2}\left|\sum_{\vec{k},s,r,\lambda,r',\lambda'}a^2\frac{2M\Delta}{\hbar^2}\right.$$

$$\left.\times\langle -|V_r^{(\lambda)}|-'\rangle\langle +'|V_{r'}^{(\lambda')}|-\rangle F_r^{(\lambda)}(\vec{k},s)F_{r'}^{(\lambda')}(\vec{k}',s')\delta(\Delta-h\omega_{\vec{k},s})\right|^2, \quad \text{(A7)}$$

where we have used $\langle +'|V_r^{(\lambda)}|+\rangle=-\langle -|V_r^{(\lambda)}|-'\rangle$ as proved in Eq. (B7) of CR.

CR define a quantity [(A6) of CR]

$$j^{\dagger}_{r\lambda,r'\lambda'}(\omega)=\int_{-\infty}^{0}d\tau\,e^{-i\omega t}\,\mathrm{Tr}(\rho_L e^{iH_L\tau/\hbar}Q_r^{(\lambda)}e^{-iH_L\tau/\hbar}Q_{r'}^{(\lambda')}),$$

where ρ_L, H_L are phonon density matrix and phonon Hamiltonian, respectively. The above equation can be reduced to

$$j^{\dagger}_{r\lambda,r'\lambda'}(\omega)=\sum_{\vec{k},s}\pi n(\omega)F_r^{(\lambda)}(\vec{k},s)F_{r'}^{(\lambda')}(\vec{k},s)\delta(\omega_{\vec{k},s}-\omega)\delta_{r,r'},$$

where $\delta_{r,r'}$ is a Kronecker's delta. This quantity is defined in CR as

$$j^{\dagger}_{r\lambda,r'\lambda'}(\omega)\equiv n(\omega)C_{\lambda\lambda'}(\omega)\delta_{r,r'}.$$

Therefore

$$C_{\lambda\lambda'}(\Delta/\hbar)=\sum_{\vec{k},s}\pi F_r^{(\lambda)}(\vec{k},s)F_r^{(\lambda')}(\vec{k},s)\delta(\omega_{\vec{k},s}-\Delta/\hbar).$$

Using this, we can rewrite (A7) as

$$\mathrm{II}=(-1)^{2M_s}16n(\Delta)\frac{\hbar\Gamma}{(\hbar\omega_{43})^2+\Gamma^2}\,|T^{\dagger}_{13,41}(\Delta/\hbar)|^2,$$

where

$$T^{\dagger}_{13,41}(\Delta/\hbar)=\frac{n(\Delta)}{\hbar^2}\sum_{\lambda\lambda' r}C_{\lambda\lambda'}(\Delta/\hbar)\langle -|V_r^{(\lambda)}|-'\rangle\langle +'|V_r^{(\lambda')}|-\rangle.$$

Defining $T^{\dagger}_{13,41}(\Delta/\hbar)=(C/2)n(\Delta)$ [(B7) of CR] and using (A5) and (A6) we find

$$\mathrm{II}=(-1)^{2M_s}4n(\Delta)\frac{B_1+B_2}{\omega_{43}^2+(B_1+B_2)^2}|C|^2.$$

Finally we obtain the desired result

$$\frac{1}{T_{10}}=\frac{4B_1B_2}{B_1+B_2}n(\Delta)\left[1+(-1)^{2M_s}\frac{|C|^2}{B_1B_2}\left(1+\frac{\omega_{43}^2}{(B_1+B_2)^2}\right)^{-1}\right], \quad \text{(A8)}$$

which is identical to (48) of CR for the case of Kramers ions. We note that this result is derived without using the Debye or long-wavelength approximation.

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