

## Comments on Spin-Lattice Relaxation

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Microscopic interpretations of an experiment measuring the temperature dependence of spin-lattice relaxation in rare-earth salts are discussed with the aid of a systematic general formalism. The discussion clarifies the relation between "two-step" phonon relaxation processes and resonant phonon-scattering processes, both of which have been proposed in the literature, to explain the experimental results. We show that a complete treatment of the two-step process—that is, a process involving two consecutive single-phonon direct processes—includes the results previously ascribed to resonant scattering processes and, in addition, gives small corrections to the reported results.

### 1. INTRODUCTION

IN a recent paper<sup>1</sup> Finn, Orbach, and Wolf proposed a two-step relaxation process to explain the rapid temperature dependence they observed in spin-lattice relaxation measurements of rare-earth salts. A similar mechanism had previously been suggested by Lloyd and Pake to describe spin relaxation in free-radical solutions.<sup>2</sup> As part of a more general discussion of relaxation processes in rare-earth salts, Orbach subsequently associated particular elements of a perturbative development of a scattering matrix with the two-step process in the hope of clarifying its microscopic physical origin.<sup>3</sup> A similar analysis was independently carried out by Aminov.<sup>4</sup> Both authors found that the process of Finn *et al.* stemmed mathematically from a divergent resonance appropriate to phonon scattering. Both resolved their divergence difficulties by utilizing techniques appropriate to resonance fluorescence.<sup>5</sup> Using systematic divergence-free methods which avoid line-width ambiguities present in the resonance-fluorescence approach, we have recently reconsidered the two-step relaxation problem and have found small corrections to the previous results. More important, our equations clarify the distinction between the resonant scattering processes of Orbach and Aminov and the nonresonant Raman process treated by Van Vleck and others.<sup>6</sup> The resonant two-phonon process of Orbach and Aminov corresponds in Van Vleck's usage to two successive one-phonon "direct" processes. The intrinsically two-phonon Raman process of Van Vleck has its counterpart in nondivergent terms of the Orbach-Aminov expressions.

While both Orbach and Aminov were able to reproduce the results of the simple model of Finn *et al.*, their scattering method made little apparent contact with

the physically more appealing two-step model of the earlier papers.<sup>1,2</sup> Such contact would be potentially useful in treating more complicated systems. It is our belief that a satisfactory microscopic analysis must be systematic, self-contained, and divergence free. It must also suggest simple physical models insofar as they apply. It is a significant and gratifying fact, therefore, that our general method reproduces the simple rate equations used by Finn *et al.*

In deriving our results, we have used an operator formalism which makes direct contact with experiment and which unambiguously specifies time ordering and integration-contour orientation in intermediate mathematical steps. It is our belief that the general use of this formalism, based upon recent progress in the theoretical analysis of quantum many-body problems,<sup>7</sup> would be highly profitable in the analysis of the dynamic interactions between localized impurities in solids and the periodic lattice (phonons), where heretofore it has been little employed.

For the purpose of the present paper it is sufficient to restrict our considerations to a simple three-level impurity in interaction with a set of Debye-model acoustic phonons. The energy-level diagram of the impurity system in the absence of dynamic lattice (phonon)-impurity interactions is indicated in Fig. 1. Also indicated is the phonon Debye energy, the max-

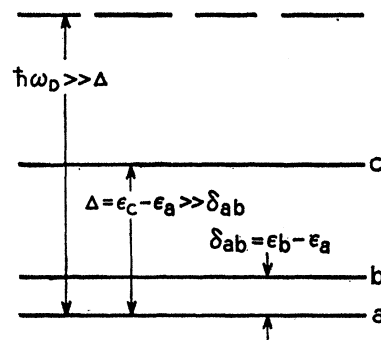


FIG. 1. Energy-level diagram of impurity system in static crystal field. The maximum phonon energy  $\hbar\omega_D$  is also indicated.

<sup>1</sup> C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **77**, 261 (1961).

<sup>2</sup> J. P. Lloyd and G. E. Pake, Phys. Rev. **94**, 579 (1954).

<sup>3</sup> R. Orbach, Proc. Phys. Soc. (London) **77**, 821 (1961); Proc. Roy. Soc. (London) **A264**, 458 (1961).

<sup>4</sup> L. K. Aminov, Zh. Eksperim. i Teor. Fiz. **42**, 783 (1962) [translation: Soviet Phys.—JETP **15**, 547 (1962)].

<sup>5</sup> W. Heitler, *The Quantum Theory of Radiation* (Clarendon Press, Oxford, 1954), p. 196.

<sup>6</sup> I. Waller, Z. Physik **79**, 370 (1932); M. Fierz, Physica **5**, 433 (1938); J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

<sup>7</sup> P. C. Martin and J. Schwinger, Phys. Rev. **115**, 1342 (1959); L. Van Hove, N. M. Hugenholtz, and L. P. Howland, *Problems in the Quantum Theory of Many-Particle Systems* (W. A. Benjamin, Inc., New York, 1961); D. J. Thouless, *The Quantum Mechanics of Many-Body Systems* (Academic Press Inc., New York, 1961).

imum acoustic-phonon energy

$$\hbar\omega_D \equiv \hbar vk_D, \quad (1.1)$$

where  $v$  is the (assumed isotropic) velocity of sound in the crystal. The Debye energy is assumed to be much greater than the level spacings

$$\Delta \equiv \mathcal{E}_c - \mathcal{E}_a \gg \mathcal{E}_b - \mathcal{E}_a \equiv \delta_{ab}. \quad (1.2)$$

For a system of this same general type Finn *et al.* observed experimentally a low-temperature relaxation process between levels  $a$  and  $b$  whose lifetime was proportional to  $\exp(\Delta/kT)$ . Remarking that the number of phonons having the energy  $\Delta$  is given by

$$\rho(\Delta) \left( \frac{1}{e^{\Delta/kT} - 1} \right) \xrightarrow{kT \ll \Delta} \rho(\Delta) e^{-\Delta/kT}, \quad (1.3a)$$

they surmise that the observed relaxation process proceeded through the level  $c$  by the absorption of a phonon of energy  $(\mathcal{E}_c - \mathcal{E}_{a,b})$  and the subsequent independent emission of a second phonon of energy  $(\mathcal{E}_c - \mathcal{E}_{b,a})$ . With  $\delta_{ab} \ll \Delta$  the probability for the absorption process is proportional to the number of phonons (1.3a) and the emission process to

$$\rho(\Delta) \left( 1 + \frac{1}{e^{\Delta/kT} - 1} \right) \xrightarrow{kT \ll \Delta} \rho(\Delta). \quad (1.3b)$$

The over-all probability for the two-step process has the temperature dependence they observed and, as they indicated in their paper, the correct order of magnitude. Our results support their original physical explanation and clarify the distinction between the two-step process they require and Van Vleck's two-phonon Raman process.

Orbach<sup>3</sup> and Aminov<sup>4</sup> analyzed the two-step relaxation problem by using what was essentially scattering theory. Given a thermal flux of incoming phonons, they computed the required  $a \rightarrow b$  transition rate from the phonon inelastic scattering cross section. The specific cross section they utilized was that appropriate to processes in which an impurity in state  $a$  scatters an incoming phonon of momentum  $\mathbf{k}$  into some outgoing momentum  $\mathbf{k}'$  and simultaneously changes its state from  $a$  to  $b$ . Treating the phonon-impurity interaction as a small scattering perturbation, they restricted themselves initially to two-phonon processes—that is, to processes having one incoming and one outgoing phonon but no additional intermediate-state phonons.

If  $\hbar\omega_D < \Delta$  so that the impurity state  $c$  centers the cross-section calculation only through *virtual* (energy nonconserving) intermediate-state  $a \rightarrow c \rightarrow b$  transitions, these processes correspond to familiar phonon Raman processes. However, when  $\hbar\omega_D > \Delta$ , as it is in the experimental situation of Finn *et al.*, the possibility exists that *real* (energy conserving) intermediate-state

transitions occur. While relaxation processes having such transitions are in a certain general sense also Raman processes, they have a second interpretation which in many circumstances is more illuminating. They can be viewed as processes in which an incoming phonon excites the impurity from state  $a$  to state  $c$ , the intermediate state  $c$  persists for some average lifetime, and the state  $c$  subsequently decays to  $b$  with the emission of an appropriate outgoing phonon. The extent to which this process is perturbed by other interactions clearly depends upon the ratio of the state  $c$  lifetime to the characteristic time of the additional perturbations.

Computing the scattering cross section by perturbation theory (by expanding in powers of the phonon-impurity interaction), Orbach and Aminov found that the real intermediate-state transitions generated a divergence in the transition probability similar to that which occurs in the study of resonance fluorescence. Physically this divergence stems from the fact that in their perturbation theory *the intermediate state  $c$  has an infinite lifetime*. They removed the divergence by replacing the infinite lifetime by a finite lifetime  $(\Gamma_c^{-1})$  appropriate to the phonon-interacting impurity state  $c$ . While this procedure is physically reasonable, it is not fully systematic and omits certain small corrections.

In Sec. 2 we introduce a specific Hamiltonian for our impurity-phonon system and define the functions of experimental interest. In the next section we derive expressions for those functions in a type of perturbation theory. In Sec. 4 we discuss the two-phonon Raman terms of the Van Vleck type and demonstrate their well-behaved nondivergent character. In Sec. 5 we neglect the intrinsically two-phonon processes and develop an appropriate solution of our equations which casts new light on the one-phonon direct processes. This solution displays the behavior required by the experimental data of Finn *et al.*

## 2. MATHEMATICAL SPECIFICATION OF PROBLEM

In this paper we concern ourselves with the following especially simple Hamiltonian ( $\hbar \equiv 1$  in all subsequent expressions):

$$\mathfrak{H} = \sum_{\mu=a,b,c} \mathcal{E}_\mu \psi_\mu^\dagger \psi_\mu + \sum_{\mathbf{k}} vk (a_{\mathbf{k}}^\dagger a_{\mathbf{k}} + \frac{1}{2}) + S(0)^0 \sum_{\mu,\mu'=a,b,c} C_{\mu\mu'} \psi_{\mu'}^\dagger \psi_\mu, \quad (2.1a)$$

where

$$C_{\mu\mu'} = C_{\mu'\mu}^*, \quad C_{ab} = 0, \quad (2.1b)$$

and where

$$S(\tau)^0 \equiv \sum_{\mathbf{k}} (k/2v)^{1/2} (a_{\mathbf{k}} e^{-ivk\tau} + a_{\mathbf{k}}^\dagger e^{ivk\tau}). \quad (2.1c)$$

The operator  $S(\tau)^0$  is related to the magnitude of the dynamic lattice strain field at the impurity. The phonon operators  $a_{\mathbf{k}}$ ,  $a_{\mathbf{k}}^\dagger$  are defined only for  $|\mathbf{k}| < k_D$  and

satisfy the familiar Bose-Einstein commutation relations

$$\begin{aligned} [a_{\mathbf{k}}, a_{\mathbf{k}'}] &= [a_{\mathbf{k}}^\dagger, a_{\mathbf{k}'}^\dagger] = 0, \\ [a_{\mathbf{k}}, a_{\mathbf{k}'}^\dagger] &= \delta(\mathbf{k}, \mathbf{k}'). \end{aligned} \quad (2.2a)$$

We define the impurity fields  $\psi, \psi^\dagger$  such that similarly<sup>8</sup>

$$\begin{aligned} [\psi_\mu, \psi_{\mu'}] &= [\psi_\mu^\dagger, \psi_{\mu'}^\dagger] = 0, \\ [\psi_\mu, \psi_{\mu'}^\dagger] &= \delta(\mu, \mu'). \end{aligned} \quad (2.2b)$$

We implicitly concern ourselves with large volume  $V$  phonon systems for which the approximation  $\sum_{\mathbf{k}} = V \int (dk)/(2\pi)^3$  obtains.

Assuming that the *phonon* field may be described by a temperature  $T \equiv (k\beta)^{-1}$ , we introduce a (nonsubscripted) expectation value  $\langle \dots \rangle$  to designate averages with respect to the thermal phonon ensemble *in the absence of an impurity*. It has the following properties<sup>7</sup>:

$$\langle \psi_\mu^\dagger \dots \rangle = \langle \dots \psi_\mu \rangle = 0, \quad \text{for } \mu = a, b, c; \quad (2.3a)$$

$$\langle a_{\mathbf{k}_1}^\dagger \dots a_{\mathbf{k}_m}^\dagger a_{\mathbf{k}_1} \dots a_{\mathbf{k}_n} \rangle = 0, \quad \text{if } n \neq m; \quad (2.3b)$$

$$\langle a_{\mathbf{k}}^\dagger a_{\mathbf{k}} \rangle = \delta(\mathbf{k}, \mathbf{k}') \frac{1}{e^{\beta v k} - 1} \equiv \delta(\mathbf{k}, \mathbf{k}') n_k; \quad (2.3c)$$

$$\begin{aligned} \langle a_{\mathbf{k}_1}^\dagger a_{\mathbf{k}_2}^\dagger a_{\mathbf{k}_2} a_{\mathbf{k}_1} \rangle &= n_{\mathbf{k}_1} n_{\mathbf{k}_2} \delta(\mathbf{k}_1 + \mathbf{k}_2, \mathbf{k}_1' + \mathbf{k}_2') \\ &\quad \times [\delta(\mathbf{k}_1, \mathbf{k}_1') + \delta(\mathbf{k}_1, \mathbf{k}_2')]; \end{aligned} \quad (2.3d)$$

etc. If at some initial time  $t=0$  the impurity is in the state  $\mu_0 = a, b, \text{ or } c$  and the phonons are thermally distributed, the probability of finding the impurity in the state  $\mu = a, b, \text{ or } c$  at any subsequent time  $t > 0$  is given by

$$\begin{aligned} P(\mu\mu', \mu_0\mu_0'; t) &\equiv \langle \psi_{\mu_0}(0) (\psi_\mu^\dagger \psi_{\mu'}) (t) \psi_{\mu_0'}^\dagger(0) \rangle \\ &\equiv \langle (\psi_\mu^\dagger \psi_{\mu'}) (t) \rangle_{\mu_0\mu_0'}, \end{aligned} \quad (2.4)$$

with  $\mu' = \mu$  and  $\mu_0' = \mu_0$ . It is convenient to group the functions (2.4) into a  $9 \times 9$  matrix  $\mathcal{O}(t)$ ,

$$[\mathcal{O}(t)]_{(\mu\mu')(\mu_0\mu_0')} = P(\mu\mu', \mu_0\mu_0'; t). \quad (2.5)$$

In the remainder of this paper we shall be concerned with the calculation of the elements of this matrix.

It is useful to supplement Eq. (2.5) with a number of additional definitions. We define the noninteracting analog  $\mathcal{O}(t)^0$  of  $\mathcal{O}(t)$  such that

$$\begin{aligned} [\mathcal{O}(t)^0]_{(\mu\mu')(\mu_0\mu_0')} &= \exp[i(\mathcal{E}_\mu - \mathcal{E}_{\mu'})t] \delta(\mu, \mu_0) \delta(\mu', \mu_0'). \end{aligned} \quad (2.6)$$

We also define the  $9 \times 9$  Hermitian coupling matrices

$$[\mathbf{C}_\pm]_{(\mu\mu')(\nu\nu')} = \begin{cases} C_{\mu'\nu'} \delta(\mu, \nu) \\ C_{\mu\nu} \delta(\mu', \nu') \end{cases}. \quad (2.7)$$

<sup>8</sup> We only consider states for which  $n_\mu \equiv \psi_\mu^\dagger \psi_\mu = 0, 1$  so that we could equivalently define the fields  $\psi, \psi^\dagger$  by commutation or anticommutation relations. To avoid sign complications we choose the former.

[The definitions (2.6) and (2.7) depend upon our assumed forms (2.1) for  $\mathcal{H}$ .] It is also convenient for our subsequent analysis to introduce the Laplace transforms  $\mathbf{P}(s)$  and  $\mathbf{P}(s)^0$  of  $\mathcal{O}(t)$  and  $\mathcal{O}(t)^0$ , respectively. For  $\text{Re}s > 0$  we have typically

$$[\mathbf{P}(s)^0]_{(\mu\mu')(\mu_0\mu_0')} \equiv \int_0^\infty dt e^{-st} [\mathcal{O}(t)^0]_{(\mu\mu')(\mu_0\mu_0')}, \quad (2.8a)$$

$$= (s + i\mathcal{E}_{\mu'} - i\mathcal{E}_\mu)^{-1} \delta(\mu, \mu_0) \delta(\mu', \mu_0'). \quad (2.8b)$$

As the phonon-impurity interaction in (2.1) gradually becomes more important, the poles (2.8b) will in  $\mathbf{P}(s)$  be displaced in the  $s$  plane and be joined by increasingly more important phonon-induced branch lines. In the resonance experiments implicitly of interest, the sharp-line transitions are described by the pole terms and not by the very broad (energy spread on the order of  $\omega_D$ ) branch lines. In the next section we develop a perturbative expansion of those pole locations.

### 3. APPROXIMATE EQUATIONS FOR THE MATRIX $\mathbf{P}(s)$

If  $\Theta$  is an arbitrary operator and if  $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1$ , then it is easy to verify by differentiation that

$$\Theta(t) = \Theta(t)^0 + i \int_0^t dt' ([\mathcal{H}_1, \Theta(t-t')^0]) (t'), \quad (3.1a)$$

where

$$\begin{aligned} \Theta(t) &\equiv \exp(i\mathcal{H}t) \Theta \exp(-i\mathcal{H}t), \\ \Theta(t)^0 &\equiv \exp(i\mathcal{H}_0 t) \Theta \exp(-i\mathcal{H}_0 t), \\ \{\Theta(t')^0\} (t) &\equiv \exp(i\mathcal{H}t) [\exp(i\mathcal{H}_0 t') \Theta \exp(-i\mathcal{H}_0 t')] \\ &\quad \times \exp(-i\mathcal{H}t), \text{ etc.} \end{aligned} \quad (3.1b)$$

Applying this identity successively, we can establish a perturbative expansion of the matrix function  $\mathcal{O}(t)$  in powers of the phonon-impurity interaction matrices (2.7). The formal expressions simplify if we note first that with  $\langle \dots \rangle$  defined as above and with  $A$  an arbitrary function of  $a_{\mathbf{k}}, a_{\mathbf{k}}^\dagger$ , but independent of  $\psi, \psi^\dagger$ ,

$$\begin{aligned} \sum_{\mu, \mu'} C_{\mu'\mu} \langle ([S\psi_\mu^\dagger \psi_{\mu'}, A\psi_{\nu'}^\dagger \psi_{\nu'}]) (t) \rangle_{\bar{\mu}\bar{\mu}'} \\ = - \sum_{\mu, \mu'} \{ [\mathbf{C}_+]_{\nu\nu', \mu\mu'} \langle (AS\psi_\mu^\dagger \psi_{\mu'}) (t) \rangle_{\bar{\mu}\bar{\mu}'} \\ - [\mathbf{C}_-]_{\nu\nu', \mu\mu'} \langle (SA\psi_\mu^\dagger \psi_{\mu'}) (t) \rangle_{\bar{\mu}\bar{\mu}'} \}. \end{aligned} \quad (3.2)$$

The first few terms of the  $\mathcal{O}(t)$  expansion are

$$\begin{aligned} \mathcal{O}(t) &= \mathcal{O}(t)^0 - \int_0^t dt' \int_0^{t'} dt'' \mathcal{O}(t-t')^0 (\mathbf{C}_+ - \mathbf{C}_-) \mathcal{O}(t'-t'')^0 \\ &\quad \times [\mathbf{C}_+ \langle S(t')^0 S(t'')^0 \rangle - \mathbf{C}_- \langle S(t'')^0 S(t')^0 \rangle] \\ &\quad \times \mathcal{O}(t'')^0 + \dots, \end{aligned} \quad (3.3)$$

or, equivalently, for  $s$  in the right half plane,

$$\begin{aligned}
\mathbf{P}(s) &= \mathbf{P}(s)^0 - \mathbf{P}(s)^0(\mathbf{C}_+ - \mathbf{C}_-) \frac{4\pi V}{(2\pi)^3} \int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) [\mathbf{P}(s+ivk)^0 \mathbf{C}_+ - \mathbf{P}(s-ivk)^0 \mathbf{C}_-] \mathbf{P}(s)^0 + \dots, \\
&= \left\{ [\mathbf{P}(s)^0]^{-1} + (\mathbf{C}_+ - \mathbf{C}_-) \frac{4\pi V}{(2\pi)^3} \int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) [\mathbf{P}(s+ivk)^0 \mathbf{C}_+ - \mathbf{P}(s-ivk)^0 \mathbf{C}_-] \right. \\
&\quad - (\mathbf{C}_+ - \mathbf{C}_-) \left( \frac{4\pi V}{(2\pi)^3} \right)^2 \int_{-k_D}^{k_D} dk dk' \frac{k^3 k'^3}{2v 2v} (1+n_k)(1+n_{k'}) \\
&\quad \times \{ [\mathbf{P}(s+ivk)^0 (\mathbf{C}_+ - \mathbf{C}_-) [\mathbf{P}(s+ivk+ivk')^0 \mathbf{C}_+ - \mathbf{P}(s+ivk-ivk')^0 \mathbf{C}_-] \mathbf{P}(s+ivk)^0 \mathbf{C}_+ - \mathbf{P}(s-ivk)^0 (\mathbf{C}_+ - \mathbf{C}_-) \\
&\quad \times [\mathbf{P}(s-ivk+ivk')^0 \mathbf{C}_+ - \mathbf{P}(s-ivk-ivk')^0 \mathbf{C}_-] \mathbf{P}(s-ivk)^0 \mathbf{C}_- \} \\
&\quad + \{ \mathbf{P}(s+ivk)^0 (\mathbf{C}_+ - \mathbf{C}_-) [\mathbf{P}(s+ivk+ivk')^0 \mathbf{C}_+ \mathbf{P}(s+ivk')^0 \mathbf{C}_+ - \mathbf{P}(s+ivk-ivk')^0 \mathbf{C}_+ \mathbf{P}(s-ivk')^0 \mathbf{C}_- \\
&\quad - \mathbf{P}(s-ivk)^0 (\mathbf{C}_+ - \mathbf{C}_-) [\mathbf{P}(s-ivk+ivk')^0 \mathbf{C}_- \mathbf{P}(s+ivk)^0 \mathbf{C}_+ - \mathbf{P}(s-ivk-ivk')^0 \mathbf{C}_- \mathbf{P}(s-ivk)^0 \mathbf{C}_-] \} + \dots \left. \right\}^{-1}. \quad (3.4)
\end{aligned}$$

The last form of (3.4) is accurate through terms of the second order in  $\mathbf{C}_\pm$ . It differs from (3.3) and the first form of (3.4) in that it is a perturbative expansion of  $[\mathbf{P}(s)]^{-1}$  while the former equations are expansions of  $\mathbf{P}(s)$ . While we do not expect direct expansions of  $\mathbf{P}(s)$  in powers of  $\mathbf{C}_\pm$  to converge in the neighborhood of the  $s$  plane poles of  $\mathbf{P}(s)$ , we do expect the expansion of  $[\mathbf{P}(s)]^{-1}$  to converge.<sup>9</sup> In our present case those poles are the  $s$ -plane zeros of

$$\begin{aligned}
D(s) &\equiv \det \left\{ [\mathbf{P}(s)^0]^{-1} \right. \\
&\quad + (\mathbf{C}_+ - \mathbf{C}_-) \frac{4\pi V}{(2\pi)^3} \int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) \\
&\quad \left. \times [\mathbf{P}(s+ivk)^0 \mathbf{C}_+ - \mathbf{P}(s-ivk)^0 \mathbf{C}_-] - \dots \right\}. \quad (3.5)
\end{aligned}$$

#### 4. THE TWO-PHONON "RAMAN" TERMS

The second-order terms of (3.4) describe what one might reasonably call the *two-phonon processes*. There are two distinct types of second-order terms in (3.4), those of the type

$$\begin{aligned}
(\dots) \mathbf{P}(s \pm ivk)^0 (\dots) \mathbf{P}(s \pm ivk \pm ivk')^0 (\dots) \\
\times \mathbf{P}(s \pm ivk)^0 (\dots), \quad (4.1a)
\end{aligned}$$

<sup>9</sup> The most important rearrangement of terms to insure convergence is that which we have indicated in (3.4). As the strength of the phonon-impurity coupling increases, additional rearrangements may be necessary. For example, one could systematically select those higher order terms which serve to convert all positive powers of  $\mathbf{P}(s \pm ivk \pm \dots)^0$  in (3.4) into  $\mathbf{P}(s \pm ivk \pm \dots)$ . This rearrangement would reduce the number of terms of each order in (3.4); however, the resulting equation would be highly nonlinear. Physically, this second rearrangement would remove the irrelevant references to the initial poles (2.8b) and would insure that only the physically relevant real singularities were taken into account.

and those of the type<sup>10</sup>

$$\begin{aligned}
(\dots) \mathbf{P}(s \pm ivk)^0 (\dots) \mathbf{P}(s \pm ivk \pm ivk')^0 (\dots) \\
\times \mathbf{P}(s \pm ivk')^0 (\dots). \quad (4.1b)
\end{aligned}$$

Both types generate Raman contributions to (3.4) and (3.5), but only terms of the type (4.1a) could display a second-order divergence similar to that in the discussions of Orbach and Aminov.<sup>3,4</sup> Since it is not the purpose of this paper to present an elaboration of familiar aspects of relaxation theory, we shall not attempt to obtain a complete second-order solution of (3.5) nor to discuss the straightforward Raman components of (4.1) which yield results equivalent to those of other authors.<sup>6</sup> Rather, we shall concentrate in this section upon determining whether divergences occur in terms of the type (4.1), and in the next section demonstrate that the process of Finn *et al.* is contained in the first-order terms of (3.4).

For  $s$  in the right half plane<sup>11</sup> we have, from (2.8) and (3.4), that to within constant factors a typical "potentially divergent" term of the type (4.1a) is

$$\begin{aligned}
\int_{-k_D}^{k_D} dk dk' k^3 k'^3 (1+n_k)(1+n_{k'}) \frac{1}{s+ivk+i(\mathcal{E}_c - \mathcal{E}_a)} \\
\times \frac{1}{s+ivk+ivk'+i(\mathcal{E}_b - \mathcal{E}_a)} \frac{1}{s+ivk+i(\mathcal{E}_c - \mathcal{E}_a)}. \quad (4.2)
\end{aligned}$$

Using the definitions  $\mathcal{E}_c - \mathcal{E}_a \equiv \Delta$ ,  $\mathcal{E}_b - \mathcal{E}_a \equiv \delta_{ab}$ , and the

<sup>10</sup> Orbach [Eq. (30) ff. in reference 2 of footnote 3] considers only processes of the first type.

<sup>11</sup> In going from (3.3) to (3.4) the restriction  $\text{Re}s > 0$  is required in order that one can carry out the interchange of time and frequency integrations necessary to reduce the time convolution integrals to products of Laplace transforms.

definition (2.3c) of  $n_k$ , we have upon making the replacement  $s = +\epsilon - i\omega$ ,  $\epsilon > 0$ ,

$$\int_{-k_D}^{k_D} dk dk' k^3 k'^3 (1+n_k) n_{k'} \frac{1}{[(\omega - vk - \Delta) + i\epsilon]^2} \frac{1}{(\omega - vk + vk' - \delta_{ab}) + i\epsilon} \tag{4.3a}$$

$$\begin{aligned} &= \frac{\partial}{\partial \Delta} \int_{-k_D}^{k_D} dk dk' k^3 k'^3 (1+n_k) n_{k'} \left\{ i \left[ \frac{P}{\omega - vk - \Delta} \frac{P}{\omega - vk + vk' - \delta_{ab}} + \pi^2 \delta(\omega - vk - \Delta) \delta(\omega - vk + vk' - \delta_{ab}) \right] \right. \\ &\quad \left. + \pi \left[ \frac{P}{\omega - vk - \Delta} \delta(\omega - vk + vk' - \delta_{ab}) - \delta(\omega - vk - \Delta) \frac{P}{\omega - vk + vk' - \delta_{ab}} \right] \right\}. \tag{4.3b} \end{aligned}$$

In going from (4.3a) to (4.3b), we used the fact that with  $\epsilon > 0$  all integrals are defined, converge without difficulty, and permit the  $\Delta$  differentiation to be removed from within the integral sign. The limit  $\epsilon \rightarrow 0^+$  follows only in the last step and is well defined. Notice that the results (4.3b) are well behaved *even without the introduction of c-level damping*.<sup>3,4</sup> Moreover, the real part of (4.3b), which is relevant to the relaxation rate (damping) does *not* preferentially select  $k = \Delta/v$  phonons in the term

$$\frac{P}{\omega - vk - \Delta} \delta(\omega - vk + vk' - \delta_{ab}), \tag{4.4a}$$

which is the closest analog of the special Orbach-Aminov relaxation term, but selects those phonons only in the term

$$\delta(\omega - vk - \Delta) \frac{P}{\omega - vk + vk' - \delta_{ab}}, \tag{4.4b}$$

which has the simple interpretation of being a *c*-level frequency correction of the direct one-phonon process associated with first-order terms of (3.4). The imaginary part of (4.3b) is relevant primarily to a frequency shift and is also well behaved.

**5. ONE-PHONON "DIRECT" RELAXATION PROCESSES**

Neglecting the second-order components of (3.4), we are left with the following equation describing the intrinsically one-phonon contributions to  $\mathbf{P}(s)$ :

$$\begin{aligned} \mathbf{P}(s) = & \left\{ [\mathbf{P}(s)^0]^{-1} + (\mathbf{C}_+ - \mathbf{C}_-) \frac{4\pi V}{(2\pi)^3} \int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) \right. \\ & \left. \times [\mathbf{P}(s+ivk)^0 \mathbf{C}_+ - \mathbf{P}(s-ivk)^0 \mathbf{C}_-] \right\}^{-1}. \tag{5.1} \end{aligned}$$

The inversion of the  $9 \times 9$  matrix on the right-hand side of (5.1) is straightforward and requires only sufficient perseverance. Since the general resulting expression is too complicated to permit an immediate and unambiguous physical interpretation, we restrict ourselves from the start to a simple case. We assume that  $\omega_D \gg \Delta \gg \delta_{ab}$ ,

that  $\delta_{ab}$  is much greater than the widths of the levels  $a, b, c$ , and that  $\delta_{ab}$  is much greater than the level shifts induced by the phonon-impurity interaction. At the same time,  $\delta_{ab}$  will be much greater than the typical inverse interlevel relaxation times.

With these magnitude restrictions the long time ( $t \gtrsim 1/\delta_{ab} \gg 1/\Delta \gg 1/\omega_D$ ) interlevel relaxation transients will still be accurately described if we make the approximation [cf. (2.8)]

$$\begin{aligned} & \int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) \mathbf{P}(s+ivk)_{(\mu\mu')^0} \\ & \approx + \int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) \frac{1}{\epsilon + ivk + i\mathcal{E}_{\mu'} - i\mathcal{E}_{\mu}}, \quad \epsilon = 0^+ \\ & \approx \frac{2\pi^2}{V} \gamma_{\mu\mu'} - i \frac{\omega_D^3}{6v^5}, \quad \omega_D \gg |\mathcal{E}_{\mu} - \mathcal{E}_{\mu'}|, \tag{5.2a} \end{aligned}$$

where [cf., the temperature dependence in Eq. (1.3)]

$$\gamma_{\mu\mu'} \equiv \frac{V(\mathcal{E}_{\mu} - \mathcal{E}_{\mu'})^3}{4\pi v^5} \left[ 1 + \frac{1}{\exp[(\mathcal{E}_{\mu} - \mathcal{E}_{\mu'})/kT] - 1} \right] = 0,$$

if  $\mu = \mu'$ .

The corresponding approximation for  $\mathbf{P}(s-ivk)^0$  is

$$\int_{-k_D}^{k_D} dk \frac{k^3}{2v} (1+n_k) \mathbf{P}(s-ivk)_{(\mu\mu')^0} \approx \frac{2\pi^2}{V} \gamma_{\mu'\mu} + i \frac{\omega_D^3}{6v^5}. \tag{5.2b}$$

The real components of (5.2) affect primarily the damping or relaxation rate, the imaginary components the frequency shift. The long-time interlevel relaxation transients are governed by the frequency ( $s = +\epsilon - i\omega$ ) region  $\omega \ll \delta_{ab}$ . For such  $\omega$  it follows from our previous magnitude assumptions that the components

$$[\mathbf{P}(s)]_{(\mu\mu')(\nu\nu)} \approx 0 \quad \text{for } \mu \neq \mu', \tag{5.3}$$

relative to the  $\mu = \mu'$  components.

As is clear from our discussion of Eq. (2.4), the  $(\mu\mu, \nu\nu)$  components of  $\mathbf{P}(s)$  are of immediate physical relevance in describing population relaxation. Multiply-

ing both sides of (5.1) from the left by the  $\{\cdot\cdot\cdot\}$  of the right-hand side, we obtain a set of nine coupled linear equations in the  $[\mathbf{P}(s)]_{(\mu\mu')(\nu\nu)}$  for each  $\nu$ . For  $\omega \ll \delta_{ab}$  six of those equations confirm our assertion (5.3). If

we use (5.3) to eliminate the  $\mu \neq \mu'$  elements from the other three equations, we are left for each  $\nu$  with the set of three coupled equations summarized in the matrix equation

$$\begin{bmatrix} s+2\gamma_{ac}|C_{ac}|^2 & 0 & -2\gamma_{ca}|C_{ac}|^2 \\ 0 & s+2\gamma_{bc}|C_{bc}|^2 & -2\gamma_{cb}|C_{bc}|^2 \\ -2\gamma_{ac}|C_{ac}|^2 & -2\gamma_{bc}|C_{bc}|^2 & s+2\gamma_{ca}|C_{ac}|^2+2\gamma_{cb}|C_{bc}|^2 \end{bmatrix} \mathbf{p}(s) = \mathbf{1}, \quad (5.4a)$$

where

$$[\mathbf{p}(s)]_{\mu\nu} \equiv [\mathbf{P}(s)]_{(\mu\mu')(\nu\nu)}. \quad (5.4b)$$

When we use the familiar elementary formula<sup>12</sup> to compute the one-phonon direct-process transition rates appropriate to the phonon-impurity interaction (2.1), we find that the nonzero  $\mu \rightarrow \mu'$  transition rates  $\Gamma_{\mu\mu'}$  are

$$\begin{aligned} \Gamma_{ac} &= 2\gamma_{ac}|C_{ac}|^2, & \Gamma_{bc} &= 2\gamma_{bc}|C_{bc}|^2, \\ \Gamma_{ca} &= 2\gamma_{ca}|C_{ac}|^2, & \Gamma_{cb} &= 2\gamma_{cb}|C_{bc}|^2. \end{aligned} \quad (5.5)$$

If we define  $p_\mu(t)$  as the population in level  $\mu$  at the time  $t$ , the simplest classical arguments<sup>1</sup> suggest the relaxation equations

$$\begin{aligned} \frac{\partial}{\partial t} p_a(t) &= -\Gamma_{ac} p_a(t) + \Gamma_{ca} p_c(t), \\ \frac{\partial}{\partial t} p_b(t) &= -\Gamma_{bc} p_b(t) + \Gamma_{cb} p_c(t), \\ \frac{\partial}{\partial t} p_c(t) &= \Gamma_{ac} p_a(t) + \Gamma_{bc} p_b(t) - (\Gamma_{ca} + \Gamma_{cb}) p_c(t). \end{aligned} \quad (5.6)$$

These equations are identical to within unspecified initial conditions to the matrix Eq. (5.4). We conclude that the relaxation processes required by the experimental results of Finn *et al.* are already contained in a complete treatment of one-phonon direct processes, and that new two-phonon relaxation processes are not required.

If we put  $p_a = 1$  and  $p_b = 0$  in the second and third of Eqs. (5.6) and if we neglect  $\partial p_c / \partial t$  in the last equation, we obtain the Orbach-Aminov result

$$\frac{\partial}{\partial t} p_b = \Gamma_{cb} p_c = \frac{\Gamma_{ac} \Gamma_{cb}}{\Gamma_{ca} + \Gamma_{cb}}. \quad (5.7)$$

The factor  $(\Gamma_{ca} + \Gamma_{cb})^{-1}$  is the finite level- $c$  lifetime  $\Gamma_c^{-1}$  whose importance we discussed in the introductory section. A more accurate description of the relaxation process is obtained by solving Eqs. (5.4) or (5.6). The solution of (5.6) appropriate to the  $t=0$  initial conditions

$$p_a = 1, \quad p_b = p_c = 0 \quad (5.8a)$$

is (in vector form)

$$\begin{bmatrix} p_a(t) \\ p_b(t) \\ p_c(t) \end{bmatrix} = \sum_{s=s_0, s_\pm} \frac{e^{-st}}{(s+\Gamma_{ac})(s+\Gamma_{bc}) + \Gamma_{ca}(s+\Gamma_{bc}) + \Gamma_{cb}(s+\Gamma_{ac})} \begin{bmatrix} \Gamma_{ca}(s+\Gamma_{bc}) \\ \Gamma_{cb}(s+\Gamma_{ac}) \\ (s+\Gamma_{ac})(s+\Gamma_{bc}) \end{bmatrix}, \quad (5.8b)$$

where

$$\begin{aligned} s_0 &= 0, \\ s_\pm &= -\frac{1}{2}(\Gamma_{ca} + \Gamma_{cb} + \Gamma_{ac} + \Gamma_{bc}) \pm \left\{ \frac{1}{4}(\Gamma_{ca} + \Gamma_{cb} + \Gamma_{ac} + \Gamma_{bc})^2 \right. \\ &\quad \left. - \Gamma_{ac}\Gamma_{bc} - \Gamma_{ca}\Gamma_{cb} - \Gamma_{bc}\Gamma_{ca} \right\}^{1/2}. \end{aligned} \quad (5.8c)$$

If  $\Gamma_{ac} \ll \Gamma_{ca}$  and  $\Gamma_{bc} \ll \Gamma_{cb}$ , then  $|s_+| \ll |s_-|$  with

$$s_- \rightarrow -(\Gamma_{ca} + \Gamma_{cb}),$$

$$s_+ \rightarrow -2 \frac{\Gamma_{ac}\Gamma_{cb} - \Gamma_{bc}\Gamma_{ca}}{\Gamma_{ca} + \Gamma_{cb}} = -(\Gamma_{ac} + \Gamma_{bc}); \quad \text{if } \Gamma_{ca} = \Gamma_{cb} \text{ or } \Gamma_{ac} = \Gamma_{bc}. \quad (5.9)$$

When these limiting forms obtain, it is clear that the rapidly disappearing  $s_-$  transients in (5.8) reflect what is essentially the  $c$ -level decay lifetime while the  $s_+$  transients reflect the slower  $a, b$  equilibration effects. Setting  $\exp(-s_+ t) = 1$  and  $\exp(-s_- t) = 0$  in the first time derivative of (5.8) in the limit (5.9), we obtain the Orbach-Aminov result (5.7).

<sup>12</sup> L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1955), 2nd ed., Eq. (29.12).