

Orbach Spin-Lattice Relaxation of Shallow Donors in Silicon*

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The spin-lattice relaxation rate $1/T_1$ for the exponential temperature-dependent Orbach process has been calculated assuming that the spin-flipping interaction is due to the residual spin-orbit interaction associated with the $1S-T_2$ -donor states. The Orbach rate constant is shown to depend principally on two physical parameters, the impurity spin-orbit splitting and the level width of the $1S-T_2$ states. Using the results of the infrared-absorption measurements of Zeiger and Krag on Bi and of Aggarwal and Ramdas on Sb, As, and P, reasonable agreement is found between the calculated results and the experimental measurements of Castner. The simple result found is possible because the level width, assumed due to spontaneous phonon emission, makes it unnecessary to consider the complicated details of the electron-phonon coupling between the $1S-A_1$ and $1S-T_2$ states.

I. INTRODUCTION

THE spin-lattice relaxation processes for shallow donors in Si are currently reasonably well understood except for the exponential temperature-dependent Orbach process. Careful measurements of the anisotropy of the spin-lattice relaxation rate $1/T_1$ by Feher and Wilson¹ showed the direct process to consist of the valley-repopulation effect and a one-valley effect, each with its own angular dependence. These results are in surprisingly good agreement with the calculations of Hasegawa² and Roth,³ who recognized the importance of shear strains in coupling the low-lying $1S$ valley-orbit states. Previous calculations⁴ considering only long-wavelength dilatational strains (these do not couple the $1S$ valley-orbit states) had given relaxation rates many orders of magnitude too slow. The Raman spin-relaxation processes have been shown⁵ to consist of a power-law contribution ($1/T_1 \propto H^0 T^9$) and an exponential temperature-dependent Orbach process. Calculations by Roth and Hasegawa and Nakayama⁶ of the T^9 process in which they include the impurity potential produce a result having all the correct dependences and the right order of magnitude. The good agreement obtained in this case is intimately related to the breakdown of the effective-mass approximation. In contrast to the direct process and the Raman T^9 process in P and As, the Orbach-process experimental data⁷ for P, As, Sb, and Bi show a strong dependence on the atomic number Z of the donor. This result suggests that the impurity spin-orbit interaction is responsible for the Orbach spin-lattice relaxation process. Recently infrared-absorption optical measure-

ments have given new information on the effect of the impurity spin-orbit interaction on the shallow donor states.

Krag and Zeiger⁸ have observed the weak $1S-A_1$ - $1S-T_2$ electric-dipole transition in Bi-doped Si. The transition showed two peaks split by 1 MeV (10^{-3} eV) which have been interpreted⁹ as due to a spin-orbit doublet produced by the residual effects of the large spin-orbit interaction of the Bi donors. Employing elevated temperatures ($30^\circ\text{K} < T < 80^\circ\text{K}$), several groups¹⁰ have observed optical transitions from the excited $1S-E$ and $1S-T_2$ states to the $2p_0$ and $2p_{\pm}$ donor states. These experiments have permitted a much more accurate determination of $1S-E$ and $1S-T_2$ energy levels. A very careful study of these and other optical transitions utilizing uniaxial stress techniques have led Aggarwal and Ramdas¹¹ to conclude the $1S-T_2$ state¹² is about 1.4 MeV lower in energy than the $1S-E$ state. At 30°K they also observed for the Sb donor a splitting (0.3 MeV) of the $1S-T_2$ state. This is the correct fraction of the Bi $1S-T_2$ -state splitting if the splitting were due to the residual impurity spin-orbit interaction. The above facts in combination with the Orbach $1/T_1$ results further reinforce the argument that the Orbach process is due to the impurity spin-orbit interaction.

Abraham¹³ proposed that the Orbach-process $1/T_1$ rate could be drastically reduced by the splitting of the $1S-T_2$ states by the application of uniaxial stress.

⁸ H. J. Zeiger, W. E. Krag, and L. M. Roth, Massachusetts Institute of Technology, Lincoln Laboratory Reports, July 15, 1962 (unpublished).

⁹ L. M. Roth, Massachusetts Institute of Technology, Lincoln Laboratory Report, No. 3, 1962 (unpublished).

¹⁰ F. P. Ottensmeyer, J. C. Giles, and J. W. Bichard, Can. J. Phys. **42**, 1826 (1964); R. L. Aggarwal, Solid State Commun. **2**, 163 (1964).

¹¹ R. L. Aggarwal and A. K. Ramdas, Phys. Rev. **140**, 1246 (1965).

¹² The notation of Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull, Vol. 5 (Academic Press Inc., New York, 1957) is followed in this paper. In tetrahedral symmetry the sixfold degenerate $1S$ effective-mass state splits into a singlet (A_1), a doublet (E), and a triplet (T_2). Aggarwal and Ramdas label the triplet T_1 .

¹³ A. Abraham (private communication).

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¹ D. K. Wilson and G. Feher, Phys. Rev. **124**, 1068 (1961).

² H. Hasegawa, Phys. Rev. **118**, 1523 (1960).

³ L. M. Roth, Phys. Rev. **118**, 1534 (1960); L. Roth, Massachusetts Institute of Technology, Lincoln Laboratory Reports, April 1960, (unpublished).

⁴ D. Pines, J. Bardeen, and C. P. Slichter, Phys. Rev. **106**, 489 (1957); E. Abrahams, *ibid.* **107**, 491 (1957).

⁵ T. G. Castner, Jr., Phys. Rev. **130**, 58 (1963).

⁶ Private communication.

⁷ T. G. Castner, Jr., Phys. Rev. Letters **8**, 13 (1962).

Thus when the splitting produced by the stress becomes larger than the small splitting due to the residual impurity spin-orbit interaction the orbital moment is partially quenched and the relaxation rate $1/T_1$ is significantly reduced. Preliminary experiments¹⁴ on P and As donors in Si have confirmed this behavior for small values of applied stress. For P and As donors the impurity spin-orbit splitting is too small compared with the linewidth to observe the splitting of the $1S$ - T_2 state in the infrared-absorption experiments. These results again point to the role of the spin-orbit interaction in the Orbach process.

The intent of this paper is to calculate the Orbach relaxation rate based on the residual impurity spin-orbit interaction for the zero-stress case. The rate constant $E(1/T_1 = Ee^{-E/kT})$ will be calculated in terms of two principal parameters: (1) the spin-orbit splitting Δ_{so} of the $1S$ - T_2 state due to the spin-orbit interaction associated with the impurity potential and (2) the level-widths of the $1S$ - T_2 excited states which are due to spontaneous phonon emission. By the use of level-widths one achieves a great simplification in the treatment of the electron-phonon interaction which involves unknown deformation potentials and complicated angular averages over phonon wave number for the umklapp intervalley-scattering processes. A relatively simple expression is then obtained which can be compared with the experimental data making use of the optical data on impurity spin-orbit splittings and linewidths of the $1S$ - T_2 states.

II. SHALLOW DONOR ENERGY LEVELS AND WAVE FUNCTIONS

A. Energy Levels without Spin-Orbit Interaction

The shallow donor levels are shown in Fig. 1. The optical transitions studied by the above investigators to determine the relative ordering of the $1S$ - T_2 and $1S$ - E levels are indicated. However, the only levels that need be considered for the Orbach process are the $1S$ states. These states deviate from the calculated effective-mass energy of the $1S$ state because of the impurity potential and the tetrahedral potential. The $1S$ states are described by wave functions

$$\psi_n(r) = \sum_{i=1}^6 \alpha_n^i F^i(\mathbf{r}) U_{\mathbf{k}_i}(\mathbf{r}) e^{i\mathbf{k}_i \cdot \mathbf{r}}, \quad (1)$$

where the sum is over the six conduction-band minima and the α_n coefficients are determined to satisfy tetrahedral symmetry. As shown by Kohn,¹⁵ the

¹⁴ D. Olson, Bull. Am. Phys. Soc. **11**, 186 (1966).

¹⁵ W. Kohn, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5.

$\alpha_n [\alpha_n = c_n(x, -x, y, -y, z, -z)]$ are

$$\begin{aligned} A_1 \quad \alpha_{A_1} &= [1/(6)]^{1/2} (1, 1, 1, 1, 1, 1), \\ E \quad \alpha_{E_a} &= \frac{1}{2} (1, 1, -1, -1, 0, 0) \\ &\alpha_{E_b} = [1/(12)]^{1/2} (1, 1, 1, 1, -2, -2), \\ T_2 \quad \alpha_{T_x} &= \frac{1}{\sqrt{2}} (1, -1, 0, 0, 0, 0) \\ &\alpha_{T_y} = \frac{1}{\sqrt{2}} (0, 0, 1, -1, 0, 0) \\ &\alpha_{T_z} = \frac{1}{\sqrt{2}} (0, 0, 0, 0, 1, -1). \end{aligned} \quad (2)$$

Several comments should be made about these wave functions. First, because of the large k_i ($k_i = 0.85k_{\max}$), the wave functions are highly oscillatory. Only the symmetric A_1 state has a nonzero $|\psi(0)|^2$ and it alone has a hyperfine interaction with the donor nucleus. Furthermore, for small \mathbf{r} ($\mathbf{k}_i \cdot \mathbf{r} \ll 1$) the E states are principally d -like and the T_2 states are principally p -like. If the T_2 states were pure p -like functions only the umklapp process (intervalley scattering) would couple the A_1 and T_2 states because of parity considerations. In general, however, the T_2 states will contain some d -like admixture which will also allow the intervalley process to couple the A_1 and T_2 states. Thus, for the Orbach process both intervalley and intravalley scattering play a role in determining $1/T_1$.

B. The $1S$ Energy Levels: Spin-Orbit and Zeeman Interactions

Appel¹⁶ has carefully considered relativistic effects on the $1S$ donor states in Ge and Si. In this paper we shall only be concerned with the spin-orbit effects. The Hamiltonian for the donor states will be

$$\begin{aligned} H &= H_{\text{eff. mass}} + U(r) \\ &\quad + \frac{\hbar^2}{2m^2c^2} [\text{grad } U(r) \times \mathbf{p} \cdot \mathbf{S}] + H_{\text{Zeeman}}, \end{aligned} \quad (3)$$

where the additional potential $U(r)$ the donor experiences is given by

$$U(r) = U_{\text{imp}}(r) + a(x^4 + y^4 + z^4) + bxyz. \quad (4)$$

The $U_{\text{imp}}(r)$ is the atomic potential of the donor and the other terms are crystal fields. It is noted that the tetrahedral term $bxyz$ has odd parity. By far the largest contribution to the spin-orbit interaction for the $1S$ states will come from $U_{\text{imp}}(r)$. Hence the

¹⁶ Joachim Appel, Phys. Rev. **133**, A280 (1964).

spin-orbit interaction is closely approximated by

$$H_{so} \sim \frac{\hbar^2}{2m^2c^2} \frac{1}{r} \frac{dU_{imp}(r)}{dr} \mathbf{L} \cdot \mathbf{S}. \quad (5)$$

The angular momentum \mathbf{L} in tetrahedral symmetry transforms according to the T_1 representation. The only nonzero matrix elements of H_{so} can be shown to be between the T_2 -triplet states and also between the T_2 and E states. No matrix elements of H_{so} involve the A_1 state, nor are there matrix elements within the E doublet. The E -doublet states can contain admixtures of opposite-spin states because of the nonzero $\langle T_2 | H_{so} | E \rangle$ matrix elements.¹⁷ These matrix elements could be comparable to the $\langle T_2 | H_{so} | T_2 \rangle$ matrix elements. However, as long as $\langle T_2 | H_{so} | E \rangle$ is substantially less than the $1S$ - T_2 - E energy separation, the E states will contain much less admixture of opposite-spin states than the T_2 states. Furthermore, the E states lie above the T_2 states and would have a smaller Boltzmann factor for the Orbach relaxation than the T_2 states. In this paper we assume the Orbach relaxation is due principally to the T_2 states and we neglect the effect of the E states. This assumption is supported by the Orbach spin-lattice relaxation results. The energy \mathcal{E} determined from the Orbach-relaxation temperature dependence⁷ is in much closer agreement with the A_1 - T_2 energy splitting than the larger A_1 - E splitting.¹⁰ For Sb and Bi $\langle T_2 | H_{so} | E \rangle$ could be comparable to the $1S$ - T_2 - E energy splitting and the E states might play a role in the Orbach relaxation, but certainly not a dominant role.

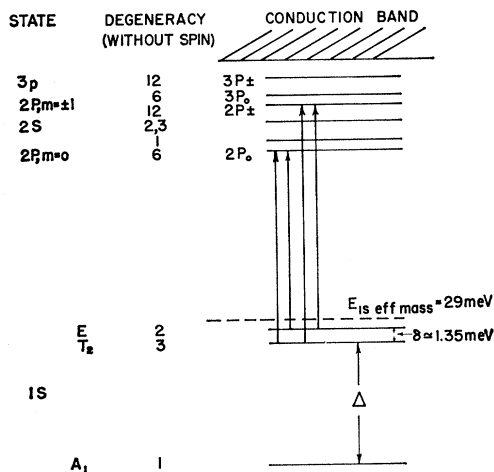


FIG. Energy-level diagram showing the orbital states of the shallow donors in silicon. The indicated optical transitions on the diagram are those studied by Aggarwal and Ramdas and also by Ottensmeyer, Giles, and Bichard. This work led to the conclusion the $1S$ - T_2 state is lower in energy than $1S$ state. Experimental results indicate the Orbach relaxation proceeds via the $1S$ - T_2 states.

¹⁷ The author is indebted to G. Watkins and F. Ham for pointing out to the author the possible importance of the spin-orbit coupling of the $1S$ - E and T_2 states. They have shown for the Li donor (interstitial instead of substitutional) that $\langle E | H_{so} | T_2 \rangle$ is larger than $\langle T_2 | H_{so} | T_2 \rangle$.

C. Diagonalization of the T_2 Energy States

The Hamiltonian (3) now becomes for a magnetic field applied in the z direction,

$$H = H_{eff, mass} + U(\mathbf{r}) + \lambda_{imp}(r) \mathbf{L} \cdot \mathbf{S} + g\mu_B H_0 S_z + \mu_B H_0 L_z, \quad (6)$$

where $\lambda_{imp} \gg \mu_B H$. It is readily shown that the orbital Zeeman term may be completely neglected. For convenience we choose our energy scale such that

$$[H_{eff, mass} + U(\mathbf{r})] |A_1\rangle = 0 |A_1\rangle$$

and

$$[H_{eff, mass} + U(\mathbf{r})] |T_2\rangle = \mathcal{E} |T_2\rangle.$$

Although

$$\langle T_2 | \lambda_{imp} \mathbf{L} \cdot \mathbf{S} | T_2 \rangle > \langle T_2 | g\mu_B H S_z | T_2 \rangle,$$

we still choose the $m_l m_s$ representation since this is consistent with the A_1 Kramer's doublet represented as pure spin states $A_1 \uparrow$ and $A_1 \downarrow$. The 6-by-6 matrix for the T_2 states breaks into two pure states, $|m_l=1, m_s=\frac{1}{2}\rangle$ and $|m_l=-1, m_s=-\frac{1}{2}\rangle$, and two 2-by-2 matrices which are readily solved yielding for the energies of the six states,

$$\begin{aligned} W &= \mathcal{E} + \beta \pm H \text{ pure-spin states,} \\ W &= \mathcal{E} + \frac{1}{2} [-\beta \pm (9\beta^2 + 4\beta H + 4H^2)]^{1/2}, \quad (7) \\ W &= \mathcal{E} + \frac{1}{2} [-\beta \pm (9\beta^2 - 4\beta H + H^2)]^{1/2}, \end{aligned}$$

where $H = \frac{1}{2} g\mu_B H_0$ and $\beta = \frac{1}{2} \langle T_{2k} | \lambda_{imp} L_j | T_{2i} \rangle$.¹⁸

For all the donors except P we have $\beta > H$. For the case $\beta \gg H$ the energy levels are shown to first order in H in Fig. 2. The wave functions showing the admixture of each spin state are also indicated in the figure. For $\beta \gg H$ the impure states become nearly equal admixtures of opposite-spin states since $a^\pm \rightarrow \sqrt{\frac{1}{3}}$ and $b^\pm \rightarrow \sqrt{\frac{2}{3}}$ as $H \rightarrow 0$. The Orbach process is represented by phonon-absorption transitions from either one of the A_1 Zeeman states to the four T_2 impure-spin states followed by phonon emission back to the other A_1 Zeeman state.

III. THE RAMAN SPIN-LATTICE RELAXATION PROCESS

Having found the energy levels of the Hamiltonian (3), the Raman spin-lattice relaxation process may be

¹⁸ It is readily shown that, assuming $F^x = F^y = F^z = (1/a^{3/2}) e^{-r/a}$

$$\beta = \frac{1}{2} \int F_y^* F_z |u_{k_0}(r)|^2 \left(\frac{dU_{imp}(r)}{dr} \right) \frac{1}{r} \sin k_0 y L_z \sin k_0 x dr$$

and we can expand $|u_{k_0}(r)|^2$ in reciprocal-lattice vectors keeping only the first constant term which is unity. Then

$$\beta \sim -\frac{K_0}{a^3} \int e^{-2r/a} \frac{1}{r} \frac{dU_{imp}(r)}{dr} y \sin k_0 y \cos k_0 x dr.$$

This integral is orders of magnitude smaller than for the isolated impurity atom both because of the oscillatory nature of the wave functions and also because of the extent of the donor wave function ($k_0 a \sim 20$) for donors in Si. The spin-orbit interaction is reduced to approximately 5×10^{-4} of the atomic value.

calculated by using second-order perturbation theory¹⁹ considering the electron-phonon interaction as the perturbation coupling the A_1 and T_2 Zeeman states. This amounts to the same approach used by Orbach²⁰ in calculating relaxation rates for rare-earth ions in crystal fields. It is different, however, in that the A_1 and T_2 states are different orbital states whereas in the rare-earth case one is considering coupling between different M_J states of a J level split by the crystal field. In the present case Orbach relaxation can proceed via all four of the impure-spin T_2 states shown in Fig. 2. The Raman spin-lattice-relaxation-transition probability associated only with the T_2 states will be given by

$$W_{A_1 \uparrow \rightarrow A_1 \downarrow} = \frac{2\pi}{\hbar^2} \int \int \left| \sum_{j=1}^4 \frac{\langle A_{1\downarrow} | H_{ep} | T_{2j} \rangle \langle T_{2j} | H_{ep} | A_{1\uparrow} \rangle}{E_{A_{1\uparrow}} - E_{T_{2j}}} \right|^2 \times \delta(\hbar\omega' - \hbar\omega - g\mu_B H) \rho(\omega) \rho(\omega') d\Omega_{\omega} d\Omega_{\omega'} d\omega d\omega', \quad (8)$$

where the summation is over the four impure-spin T_2 states and conservation of energy introduces the delta function requiring that the difference of the absorbed phonon energy $\hbar\omega$ and the emitted phonon energy $\hbar\omega'$ be equal to the Zeeman energy difference. Of course, in the second-order perturbation of H_{ep} , both orders of the two H_{ep} 's, namely absorption followed by emission and emission followed by absorption, must be considered although only the former contributes to the Orbach process.

The matrix elements $\langle T_2 | H_{ep} | A_1 \rangle$ have previously been considered⁵ and will not be fully discussed here. Although both intervalley and intravalley processes can couple the A_1 and T_2 states, the large ω_q and q required for the Orbach process produce substantial interference in the matrix elements tending to reduce the effect of intravalley scattering. This can make $\langle T_2 | H_{ep} | A_1 \rangle$ depend mostly on umklapp intervalley scattering between opposite conduction-band minima. This fact may explain why the T_2 levels apparently have little effect on the low-temperature direct and the Raman power-law spin-lattice relaxation processes.⁵ The matrix elements $\langle T_2 | H_{ep} | A_1 \rangle$ are functions of the conduction-band shear and dilatational-deformation constants Ξ_u and Ξ_d , respectively, and are also proportional to an expansion coefficient of the period part of the Bloch function and nontrivial functions of q .⁵

$$W_{A_1 \uparrow \rightarrow A_1 \downarrow} = \frac{2\pi}{\hbar^2} \int \int \left\langle \left| \langle A_{1\downarrow} | H_{ep} | T_{2\downarrow} \rangle \left\langle \frac{(T_x - iT_y)}{\sqrt{2}} \uparrow | H_{ep} | A_{1\uparrow} \right\rangle \right|^2 \right\rangle_{\Omega_{\omega q}, \Omega_{\omega' q_1}} \rho(\omega) \rho(\omega') n_{\omega q} n_{\omega' q_1} \times \left| \sum_{n=1}^4 (-1)^n a^n b^n \left(\frac{1}{H + \omega - \alpha_n} + \frac{1}{H - \omega' - \alpha_n} \right) \right|^2 \delta(\omega' - \omega - 2H) d\omega d\omega', \quad (9)$$

¹⁹ Presumably one could also use third-order perturbation theory and treat H_{so} as a perturbation as was done in the classical paper of Van Vleck treating the Raman spin-lattice relaxation processes. J. H. Van Vleck, Phys. Rev. **57**, 426 (1940). Here the exact diagonalization of the T_2 states including the spin-orbit interaction is instructive because the results will show constructive and destructive interference between the four T_2 impurespin states.

²⁰ R. Orbach, Proc. Phys. Soc. (London) **77**, 821 (1960); Proc. Roy. Soc. (London) **A264**, 458 (1961).

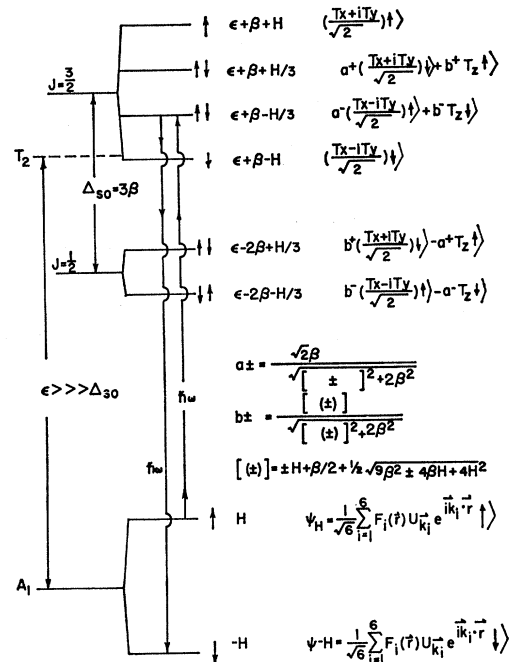


FIG. 2. Energy levels and wave functions of $1S-A_1$ and $1S-T_2$ states including the impurity spin-orbit interaction and the Zeeman energy. The four $1S-T_2$ states which are admixtures of the two spin states \uparrow and \downarrow are responsible for the Orbach relaxation. The energies are shown for $H < \beta$ to first order in H .

However, it is not necessary to evaluate the matrix elements explicitly and do the angular averages over q . All the complicated details of the electron-phonon matrix elements evaluated at phonon frequencies equal to the energy separation between the four "impure-spin" T_2 states can be lumped into a single parameter, namely Γ_p ($\Gamma_p = \hbar W_{sp}$), the level width of the T_2 levels due to spontaneous phonon emission to the donor ground state A_1 . The level widths will be a function of the $1S-A_1-1S-T_2$ energy separation but in this treatment the small second-order differences in level widths of the four impure-spin $1S-T_2$ states will be neglected and a common level width will be assumed.

Examination of the wave functions of the four impure-spin T_2 states shows that the squared matrix elements are the same for the four terms in the sum in (8). Implicitly performing the angular averages over q and putting in the thermal-phonon quantum numbers (8) becomes

where

$$a^1b^1 = a^2b^2 = a^-b^-; \quad a^3b^3 = a^4b^4 = a^+b^+ \quad (10)$$

and

$$\begin{aligned} \alpha_1 &= \mathcal{E} - 2\beta - H/3 - i\Gamma/2, \\ \alpha_2 &= \mathcal{E} + \beta - H/3 - i\Gamma/2, \\ \alpha_3 &= \mathcal{E} - 2\beta + H/3 - i\Gamma/2, \\ \alpha_4 &= \mathcal{E} + \beta + H/3 - i\Gamma/2. \end{aligned} \quad (11)$$

In the Raman integral most of the contribution comes for ω and $\omega' \gg H$ and using the delta function we may assume $\omega' = \omega$ as an excellent approximation. Consistent with this, we also neglect H in the energy denominators. The thermal-phonon quantum-number product can be set equal to $e^{-\omega/kT}$ since the integrand peaks for $\omega \gg kT$. Introducing these approximations (9) becomes

$$W_{A_1\uparrow \rightarrow A_1\downarrow} = \frac{2\pi}{\hbar^2} \int_0^{\omega_{\max}} G(\omega) e^{-\omega/kT} d\omega \left| \sum_{n=1}^4 (-1)^n a^n b^n \times \left(\frac{1}{\omega - \alpha_n} - \frac{1}{\omega + \alpha_n} \right) \right|^2, \quad (12a)$$

where

$$G(\omega) = \left\langle \left\langle A_1\downarrow | H_{\text{ep}} | T_z \downarrow \right\rangle \times \left\langle \left(\frac{T_x - iT_y}{\sqrt{2}} 1 | H_{\text{ep}} | A_1 \right) \right\rangle \right\rangle_{\Omega_{\omega_q}, \Omega_{\omega_q'}} \rho^2(\omega). \quad (12b)$$

In the general case the energy-denominator factor may be expanded in partial fractions to obtain a sum of simple first-order pole terms. The energy-denominator factor becomes

$$\left| \sum_{n=1}^4 (-1)^n a^n b^n \left(\frac{1}{\omega - \alpha_n} - \frac{1}{\omega + \alpha_n} \right) \right|^2 = \sum_{n=1}^4 \left(\frac{c_n}{\omega - \alpha_n} + \frac{c_n^*}{\omega - \alpha_n^*} + \frac{d_n}{\omega + \alpha_n} + \frac{d_n^*}{\omega + \alpha_n^*} \right), \quad (13)$$

where the c_n and d_n are a set of complex coefficients determined by the partial-fractions expansion. At this juncture we shall assume first that the latter two non-resonant terms make a negligible contribution to the Orbach process. The more general case is considered in Appendix I. A second assumption we shall make is that $H < \Gamma_p$ for all the donors which appears to be well satisfied for $H_0 \simeq 3000\text{G}$. The terms corresponding to α_1 and α_3 and also corresponding to α_2 and α_4 can then be grouped in pairs with the same energy denominator since their energy separation is smaller than the line width. This is equivalent to saying relaxation via α_1 and α_3 (also α_2 and α_4) will constructively interfere as may be seen by the signs of the different spin coefficients of the wave functions shown in Fig. 2. Correction terms, if desired, can be found from a Taylor-series expansion in the energy H . We replace α_1 and α_3 by $\lambda_1 = \mathcal{E} - 2\beta - i\Gamma/2$ and α_2 and α_4 by $\lambda_2 = \mathcal{E} + \beta - i\Gamma/2$. After this replacement in (13) each term has a common

factor $(a^+b^+ + a^-b^-)$ which may be factored out. Equation (13) then becomes

$$\left| \sum_{n=1}^4 (-1)^n a^n b^n \left(\frac{1}{\omega - \alpha_n} - \frac{1}{\omega + \alpha_n} \right) \right|^2 \simeq (a^+b^+ + a^-b^-)^2 \sum_{n=1}^2 \left(\frac{c_n'}{\omega - \lambda_n} + \frac{c_n'^*}{\omega - \lambda_n^*} \right), \quad (14)$$

where for the present case the coefficients c_1' and c_2' are

$$\begin{aligned} c_1' &= \frac{-3\beta}{i\Gamma(3\beta + i\Gamma)} = \frac{-\Delta_{\text{so}}}{i\Gamma(\Delta_{\text{so}} + i\Gamma)}, \\ c_2' &= \frac{-3\beta}{i\Gamma(3\beta + i\Gamma)} = \frac{-\Delta_{\text{so}}}{i\Gamma(\Delta_{\text{so}} - i\Gamma)}. \end{aligned} \quad (15)$$

The transition rate (12) now becomes

$$W_{A_1\uparrow \rightarrow A_1\downarrow} = \frac{2\pi}{\hbar^2} (a^+b^+ + a^-b^-)^2 \times \left[\sum_{n=1}^2 c_n' \int_0^{\omega_{\max}} \frac{G(\omega) e^{-\omega/kT} d\omega}{\omega - \lambda_n} + \text{c.c.} \right]. \quad (16)$$

Two different approaches will be presented for evaluating (16). The first is direct integration making use of the principal-value theorem while the second is simply a Taylor-series-expansion approach.

A. Direct Integration

The integrals in (16) can be readily evaluated if the Orbach peak in the integrand is much narrower in width than the nonresonant thermal peak. If we set $G(\omega) = \sum_n A_n \omega^n$ the most important term in the series will be $n=6$. In the Debye approximation $G(\omega) = A\omega^6$ for which the thermal part of the integrand will peak at $\omega = 6kT$ and have a width $\Delta\omega = 2(6)^{1/2}kT$. For all the donors the experimental evidence indicates Γ less than $kT/3$ hence $\Gamma \ll \Delta\omega$. The integrals in (16) are then closely approximated using the principal-value theorem by

$$\int_0^{\omega_{\max}} \frac{G(\omega) e^{-\omega/kT}}{\omega - \mathcal{E}_n + i\Gamma/2} \simeq P \int_0^{\omega_{\max}} \frac{G(\omega) e^{-\omega/kT}}{\omega - \mathcal{E}_n} - i\pi G(\mathcal{E}) e^{-\mathcal{E}/kT}. \quad (17)$$

Using (17) for the four integrals in (16) we collect terms and find the transition probability becomes

$$\begin{aligned} W_{A_1\uparrow \rightarrow A_1\downarrow} &= \frac{4\pi}{\hbar^2} (a^+b^+ + a^-b^-)^2 \left\{ \frac{\pi \Delta_{\text{so}}^2 e^{-\mathcal{E}/kT}}{\Gamma} \right. \\ &\quad \times [G(\mathcal{E} - 2\beta) e^{2\beta/kT} + G(\mathcal{E} + \beta) e^{-\beta/kT}] \\ &\quad + \Delta_{\text{so}} P \int_0^{\omega_{\max}} G(\omega) e^{-\omega/kT} \\ &\quad \left. \times \left(\frac{1}{\omega - (\mathcal{E} - 2\beta)} - \frac{1}{\omega - (\mathcal{E} + \beta)} \right) d\omega \right\}. \quad (18) \end{aligned}$$

The largest contribution comes from the first terms while the difference of the two principal-value integrals can be shown to be much smaller. Furthermore the latter terms introduce correction terms which consist of power-law temperature-dependent terms. We expand $G(\mathcal{E}-2\beta)$ and $G(\mathcal{E}+\beta)$ about \mathcal{E} and we also expand the exponentials in β/kT since $\beta \ll \mathcal{E}$ and $\beta < kT/3$. The result is

$$W_{A_1\uparrow \rightarrow A_1\downarrow} = \frac{8\pi^2 (a^+b^+ + a^-b^-)^2 \Delta_{so}^2}{\hbar^2 (\Delta_{so}^2 + \Gamma^2)} \frac{G(\mathcal{E})e^{-\mathcal{E}/kT}}{\Gamma} + \text{higher-order terms.} \quad (19)$$

The principal-value integral

$$P \int_0^{\omega_{\max}} G(\omega) e^{-\omega/kT} / (\omega - \mathcal{E}) d\omega$$

is readily evaluated by extending the upper limit to infinity and employing Laplace transforms.²¹ Since $kT < 0.5\omega_{\max}$ for the experimental range of interest, this is an excellent approximation. The result is

$$(-1)^{n+1} G(\mathcal{E}) d^n / dz^n [e^{-z} \text{Ei}(z)]_{z=\mathcal{E}/kT}.$$

For all the donors $z > 6$. An asymptotic expansion of $\overline{\text{Ei}}(z)$ for large z is $e^z(1/z + 1/z^2 + 2!/z^3 + \dots)$. The final result for the integral is

$$-G(\mathcal{E}) n! (kT/\mathcal{E})^{n+1} (1 + kT/\mathcal{E} + \dots)$$

Although $n! (kT/\mathcal{E})^{n+1}$ can be comparable to

$$\pi(\Delta_{so}/\Gamma) e^{-\mathcal{E}/kT}$$

the fact that (18) yields the difference of two nearly identical power-law series of terms signifies the exponential contribution is dominant. For $z=6$ the power-law contribution is only 3% of the exponential contribution. Equation (19) should be a good approximation to the Orbach-relaxation rate $W_{A_1\uparrow \rightarrow A_1\downarrow}$ due to the impurity spin-orbit interaction.

B. Taylor-Series Expansion

Writing out the transition probability (12) without expanding into partial fractions but making the other assumptions leading to (16), $W_{A_1\uparrow \rightarrow A_1\downarrow}$ becomes

$$W_{A_1\uparrow \rightarrow A_1\downarrow} = \frac{2\pi}{\hbar^2} (a^+b^+ + a^-b^-)^2 \int_0^{\omega_{\max}} G(\omega) e^{-\omega/kT} \times \left| \frac{1}{\omega - (\mathcal{E} - 2\beta - i\Gamma/2)} - \frac{1}{\omega - (\mathcal{E} + \beta - i\Gamma/2)} \right|^2 d\omega. \quad (20)$$

Now, instead of using partial fractions, multiply out the quantity within the absolute value sign in (20) and make the following three substitutions:

$$\begin{aligned} x &= \omega - (\mathcal{E} - 2\beta), \\ y &= \omega - (\mathcal{E} + \beta), \\ z &= \omega - (\mathcal{E} - \beta/2). \end{aligned} \quad (21)$$

The transition probability now becomes

$$W_{A_1\uparrow \rightarrow A_1\downarrow} = \frac{2\pi}{\hbar^2} (a^+b^+ + a^-b^-)^2 e^{-\mathcal{E}/kT} \left\{ e^{2\beta/kT} \int_{-(\mathcal{E}-2\beta)}^{\omega_{\max}-(\mathcal{E}-2\beta)} \frac{G(\mathcal{E}+2\beta+x) e^{-x/kT} dx}{x^2 + (\Gamma/2)^2} + e^{-\beta/kT} \int_{-(\mathcal{E}+\beta)}^{\omega_{\max}-(\mathcal{E}+\beta)} \frac{G(\mathcal{E}+\beta+y)}{y^2 + (\Gamma/2)^2} - e^{\beta/2kT} \int_{-(\mathcal{E}-\beta/2)}^{\omega_{\max}-(\mathcal{E}-\beta/2)} \left[\frac{G(\mathcal{E}-\beta/2+z) e^{-z/kT}}{(z-3\beta/2+i\Gamma/2)(z-3\beta/2-i\Gamma/2)} + \text{c.c.} \right] dz \right\}. \quad (22)$$

Since $\beta \ll kT$ we set the exponentials in β/kT equal to unity. Furthermore since $\beta \ll \mathcal{E}$ the functions $G(\mathcal{E}-2\beta+x)$, etc. may be replaced by $G(\mathcal{E}+x)$, etc. to a good approximation. However, the β cannot be dropped in the energy denominators. We note that for $\Gamma < kT/3$ the Lorentzian part of the integrand varies much more rapidly than $G(\mathcal{E}+x)e^{-x/kT}$. It is therefore convenient to expand $G(\mathcal{E}+x)e^{-x/kT}$ in a Taylor-series expansion.

$$G(\mathcal{E}+x)e^{-x/kT} = G(\mathcal{E}) + \left(G'(\mathcal{E}) - \frac{G(\mathcal{E})}{kT} \right) x + \left(G''(\mathcal{E}) - \frac{2G'(\mathcal{E})}{kT} + \frac{G(\mathcal{E})}{(kT)^2} \right) \frac{x^2}{2} + \dots \quad (23)$$

The limits on the integrals need not be chosen precisely for the first few terms in the Taylor expansion since the main contribution to the Orbach process comes from $|x| < \Gamma/2$. For the experimental conditions, the power-law contribution comes from negative x . Somewhat arbitrarily we shall select the limits to be a and $-a$ where $a \gg \Gamma$ ($a=10\Gamma$ would cover most of the acoustic spectrum.) Equation (22) becomes

$$W_{A_1\uparrow \rightarrow A_1\downarrow} = \frac{2\pi}{\hbar^2} (a^+b^+ + a^-b^-)^2 e^{-\mathcal{E}/kT} \sum_{n=0}^{\infty} \left[\frac{d^n}{dx^n} \left(\frac{G(\mathcal{E}+x)e^{-x/kT}}{n!} \right)_{x=0} \right] \times \left\{ 2 \int_{-a}^a \frac{x^n dx}{x^2 + (\Gamma/2)^2} - \left(\int_{-a}^a \frac{x^n dx}{(x-3\beta/2+i\Gamma/2)(x+3\beta/2-i\Gamma/2)} + \text{c.c.} \right) \right\}. \quad (24)$$

²¹ *Bateman Tables of Integral Transforms*, edited by A. Erdelyi (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, 135.

The integrals for the zeroth-order term may readily be evaluated leading to the following simple result after combining terms and using $\Delta_{so} = 3\beta$, namely,

$$W_{A_1\uparrow \rightarrow A_1\downarrow}^0 = \frac{4\pi^2}{\hbar^2} 2(a^+b^+ + a^-b^-)^2 \frac{G(\mathcal{E})e^{-\mathcal{E}/kT}}{\Gamma} \times \left(\frac{\Delta_{so}^2}{\Gamma^2 + \Delta_{so}^2} \right), \quad (25)$$

which is the same result as (19). The higher-order terms in the sum in (24) are discussed in Appendix II. We find there that the n th order terms will be proportional to $(\Gamma/kT)^{2n}$ times the zeroth-order term and will have a negligible effect if $\Gamma \ll kT$, which appears to be satisfied for all the donors. The explanation for the compact result in (25) is simply that we have made our expansion about the resonant phonons most important for the Orbach process. Inspection of the higher-order terms shows they are smallest when $kT \simeq \mathcal{E}/n$ [where $G(\omega) = A\omega^n$] but become more important for either higher or lower temperatures. To further simplify (25) we need to consider the origin of the level width.

C. Level-Width Considerations

The contribution to the level width of the T_2 states due to spontaneous phonon emission, namely Γ_p , assuming there is no interference in the phonon emission to the $A_1\uparrow$ and $A_1\downarrow$ Zeeman states is given by

$$\Gamma_p = W^{ep}\hbar = \frac{2\pi}{\hbar} \left[a^{\pm 2} \langle | \langle A_1 | H_{ep} | T_z \rangle |^2 \rangle_{\Omega_q} + b^{\pm 2} \left\langle \left| \langle A_1 | H_{ep} | \frac{T_x \pm iT_y}{\sqrt{2}} \rangle \right|^2 \right\rangle_{\Omega_q} \right] \rho(\mathcal{E}). \quad (26)$$

Using the definition of $G(\omega)$, recognizing the two matrix elements squared in (26) after performing the angular averages are the same, and recalling that $a^{\pm 2} + b^{\pm 2} = 1$, Γ_p becomes equal to $2\pi/\hbar [G(\mathcal{E})]^{1/2}$. Eliminating $G(\mathcal{E})$ in (25) and using $1/T_1 = W_{A_1\uparrow \rightarrow A_1\downarrow}^0 + W_{A_1\downarrow \rightarrow A_1\uparrow}^0$ the spin-lattice relaxation rate becomes

$$\frac{1}{T_1} = 4(a^+b^+ + a^-b^-)^2 \frac{\Gamma_p^2}{\hbar\Gamma} e^{-\mathcal{E}/kT} \left(\frac{\Delta_{so}^2}{\Gamma^2 + \Delta_{so}^2} \right). \quad (27)$$

Further consideration of the Orbach-relaxation rate involves the thorny question of level widths, the problem having arisen principally in relation to the width of the infrared-absorption lines of shallow donors. The mechanism of Lax and Burstein²² will not apply here since the transitions here only involve $1S$ states. Spontaneous phonon emission as discussed by Kane²³ appears to be a most likely candidate to contribute to the

$1S$ - T_2 level widths due to lifetime broadening. A careful analysis of the linewidth mechanisms for the infrared spectral lines of boron acceptors in silicon has been made by Colbow.²⁴ Besides phonon broadening he considers the following: (a) internal strains, (b) concentration broadening (impurity banding), (c) Stark broadening due to ionized impurities. (c) will not be important for this work because it is negligible below 30°K where the number of ionized donors will be infinitesimally small. Broadening due to internal strains will be less than 10^{-4} eV for typical dislocation densities. Concentration broadening does appear to be a possible effect and indeed the Orbach rate constants are shown to vary with concentration.⁷ However, the circumstances pertaining to the spin-lattice relaxation of the shallow donor-electron spins are not really analogous to the infrared-absorption case.

For much of the Orbach process temperature range $T_1 \ll T_2'$ ($1/T_2'$ is the static low-temperature spin-packet width). T_2' has been measured by the pulse experiments of Gordon and Bowers.²⁵ At higher temperatures where T_1 determines the spin-packet width of the inhomogeneously broadened line the different donors are relaxing independently of each other. Furthermore, the Orbach-rate constant E in (27) does not depend, except for small higher order corrections, on the energy \mathcal{E} of the resonant phonons. Any smearing of \mathcal{E} for different donors due to strains or impurity banding (static effects) should have little effect on the Orbach-rate constant E (of course the exponential term can be affected). Effects which limit the lifetime of the $1S$ - T_2 states can affect E . It is probable that at low temperatures and concentrations the individual donor level width is determined by spontaneous phonon emission so that we can set $\Gamma = \Gamma_p$ which reduces $1/T_1$ to

$$\frac{1}{T_1} = 4(a^+b^+ + a^-b^-)^2 \frac{\Gamma_p e^{-\mathcal{E}/kT}}{\hbar} \left(\frac{\Delta_{so}^2}{\Gamma_p^2 + \Delta_{so}^2} \right). \quad (28)$$

IV. DISCUSSION AND COMPARISON WITH EXPERIMENT

Equation (28) has a particularly simple and appealing form and can be interpreted physically as follows. The factor $(\Gamma_p/\hbar)e^{-\mathcal{E}/kT}$ is just the rate at which donor electrons are excited from the $1S$ - A_1 to T_2 states. A factor $2(a^+b^+ + a^-b^-)^2$ represents the effectiveness of the four impure-spin T_2 states in flipping the spins of electrons excited to the T_2 states by phonon absorption. Were it not for the constructive interference between the $(\mathcal{E} + \beta + H/3)$ and $(\mathcal{E} + \beta - H/3)$ levels and also between the $(\mathcal{E} - 2\beta + H/3)$ and $(\mathcal{E} - 2\beta - H/3)$ levels, this term would be $2[(a^+b^+)^2 + (a^-b^-)^2]$, where $(a^+b^+)^2$

²⁴ K. Colbow, Can. J. Phys. **41**, 1801 (1963).

²⁵ J. P. Gordon and K. D. Bowers, Phys. Rev. Letters **1**, 368 (1958).

²² M. Lax and E. Burstein, Phys. Rev. **100**, 592 (1955).

²³ E. O. Kane, Phys. Rev. **119**, 40 (1960).

TABLE I. Orbach-process results. $1/T_1 = Ee^{-\epsilon/kT}$.

Donor	Atomic	Δ_{so} MeV	ϵ MeV	H/β	$(a^+b^+ + a^-b^-)$	E_{max} $10^{10}/\text{sec}$	Γ_p MeV	E_{calc} $10^{10}/\text{sec}$	Donor concentration $10^{15}/\text{cc}$	E_{expt} $10^{10}/\text{sec}$
Bi	1.25	1.0 ^a	34 ^a	0.06	0.88	42.5	0.3 (est)	23.5	4	52
Sb	0.42	0.3 ^b	9.55 ^b	0.20	0.87	12.8	0.2 ^b	12	6	26
As	0.186	0.13 (est)	21.1 ^b	0.87	0.70	4.4	0.5 (est)	2.1	3	6.4
P	0.031	0.022 (est)	11.6 ^b	3.16	0.18	0.18	0.4 0.3 (est) 0.2 (est)	2.6 0.027 0.041	0.25 0.9 0.15	1.5 0.091 0.020

^a Reference 8.
^b Reference 11.

represents the fractional probability the spin is flipped in the $(\mathcal{E} + \beta + H/3)$ or $(\mathcal{E} - 2\beta + H/3)$ state, while $(a^-b^-)^2$ represents the fractional probability the spin is flipped in the $(\mathcal{E} + \beta - H/3)$ or $(\mathcal{E} - 2\beta - H/3)$ state. The remaining factor of 2 is introduced by the definition $1/T_1 = W_{A_1\uparrow \rightarrow A_1\downarrow} + W_{A_1\downarrow \rightarrow A_1\uparrow}$. The last factor is simply the interference factor measuring the destructive interference between the $(\mathcal{E} + \beta)$ T_2 states and the $(\mathcal{E} - 2\beta)$ T_2 states. For $\Delta_{so} \gg \Gamma_p$ these levels are well separated compared to the level width, there is no destructive interference, and the relaxation proceeds independently for the $(\mathcal{E} + \beta)$ and $(\mathcal{E} - 2\beta)$ levels. The relaxation rate then appears to be independent of Δ_{so} , but, of course, this is only true if $\Delta_{so} \gg H$. For $\Delta_{so} < \Gamma_p$ there is destructive interference and the relaxation rate is proportional to Δ_{so}^2/Γ_p assuming $\Delta_{so} \gg H$. Considering H and Δ_{so} fixed the Orbach rate constant E as a function of Γ_p obtains a maximum when $\Gamma_p = \Delta_{so}$. This maximum-relaxation rate is given by

$$(1/T_1)_{max} = 4(a^+b^+ + a^-b^-)^2 (\Delta_{so}/2\hbar)^2 e^{-\epsilon/kT}. \quad (29)$$

Using the measured Δ_{so} for Bi and Sb and estimated values for As and P, using $H = 0.167 \text{ cm}^{-1}$, and using Γ_p 's for the $1S-T_2$ levels based on Aggarwal and Ramdas's data¹¹ and partly on estimates of the Γ_p due to umklapp phonon emission,⁵ the Orbach rate-constants have been calculated and are shown in Table I along with the maximum values from (29) and the experimental values. The agreement between E_{calc} and E_{expt} for the low-concentration P and As samples for reasonable values of Γ_p is quite good. However, it has been assumed that the Δ_{so} for As and P can be extrapolated from the values of Δ_{so} for Sb and Bi in the same ratio as for the free atoms. This assumption may not be valid if the core parts of the impurity wave function are different for different donors. For the high-concentration samples for all the donors the E_{expt} values are two or three times larger than the E_{calc} values: However, the ratios of the E_{expt} [for example, $E_{expt}(\text{Bi})/E_{expt}(\text{Sb})$] for the approximately equivalent concentration samples are in much better agreement with the calculated ratios. A careful quantitative check of (28) would require both more precise

knowledge of the $1S-T_2$ level widths and more experimental data for $1/T_1$ for the different donors at concentrations approaching $10^{15}/\text{cc}$. At present (28) does seem to adequately describe the Orbach relaxation rate for the shallow donors in Si.

A remaining problem is that of the level width Γ_p . If the $1S-T_2$ states decay principally via the umklapp process, previous calculations⁵ have suggested there would actually be a much larger variation in the umklapp Γ_p for the $1S-T_2$ states than is apparently observed in infrared-absorption linewidths or than that which is required to give agreement of the experimental results with (28). In particular the energy separation of the $1S-A_1$ and $1S-T_2$ states for As is just right to maximize the umklapp-process phonon decay of the $1S-T_2$ states which would suggest a much larger Γ_p for As than any of the other donors. It is also worth mentioning that while at low temperatures and long phonon wavelengths the shallow-donor spin-lattice relaxation processes are due to transverse phonons; the Orbach process, utilizing only very short-wavelength phonons, is almost entirely due to longitudinal phonons.

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APPENDIX I: PARTIAL-FRACTIONS EXPANSION

Assuming constructive interference between the Zeeman states ($H < \Gamma$), we need only consider the sum in (12) to be over the $\mathcal{E} - 2\beta$ and $\mathcal{E} + \beta$ pairs of Zeeman states. The sum can now be converted to

$$\left| \sum_{n=1}^2 (-1)^n \left(\frac{1}{\omega - \lambda_n} - \frac{1}{\omega + \lambda_n} \right) \right|^2 = \left| \sum_{n=1}^4 (-1)^n \left(\frac{1}{\omega - \lambda_n} \right) \right|^2, \quad (I 1)$$

where

$$\begin{aligned} \lambda_1 &= \mathcal{E} - 2\beta - i\Gamma/2; & \lambda_4 &= -\lambda_1 \\ \lambda_2 &= \mathcal{E} + \beta - i\Gamma/2; & \lambda_3 &= -\lambda_2. \end{aligned} \quad (I 2)$$

The nonresonant terms present in the original sum are now due to poles λ_3 and λ_4 . Expansion of (II) by partial fractions gives

$$\begin{aligned} & \frac{1}{\omega - \lambda_1} \left[\frac{1}{-i\Gamma} + \frac{1}{\Delta_{so} + i\Gamma} + \frac{1}{2\mathcal{E} - \beta} - \frac{1}{2\mathcal{E} - 4\beta} \right] + \text{c.c.}, \\ & \frac{1}{\omega - \lambda_2} \left[\frac{1}{-i\Gamma} - \frac{1}{\Delta_{so} - i\Gamma} + \frac{1}{2\mathcal{E} - \beta} - \frac{1}{2\mathcal{E} + 2\beta} \right] + \text{c.c.}, \quad (\text{I } 3) \\ & \frac{1}{\omega - \lambda_3} \left[\frac{1}{i\Gamma} + \frac{1}{\Delta_{so} - i\Gamma} + \frac{1}{2\mathcal{E} + 2\beta} - \frac{1}{2\mathcal{E} - \beta} \right] + \text{c.c.}, \\ & \frac{1}{\omega - \lambda_4} \left[\frac{1}{i\Gamma} - \frac{1}{\Delta_{so} + i\Gamma} + \frac{1}{2\mathcal{E} - 4\beta} - \frac{1}{2\mathcal{E} - \beta} \right] + \text{c.c.} \end{aligned}$$

Combining the terms in the brackets by expanding the latter term-energy denominators in series for $\beta/\mathcal{E} \ll 1$ this expression becomes

$$\begin{aligned} & \frac{\Delta_{so}}{\omega - \lambda_1} \left[\frac{-1}{i\Gamma(\Delta_{so} + i\Gamma)} - \frac{1}{(2\mathcal{E} - 5\beta/2)^2} \right] + \text{c.c.}, \\ & \frac{\Delta_{so}}{\omega - \lambda_2} \left[\frac{-1}{i\Gamma(\Delta_{so} - i\Gamma)} + \frac{1}{(2\mathcal{E} + \beta/2)^2} \right] + \text{c.c.}, \\ & \frac{\Delta_{so}}{\omega - \lambda_3} \left[\frac{1}{i\Gamma(\Delta_{so} - i\Gamma)} - \frac{1}{(2\mathcal{E} + \beta/2)^2} \right] + \text{c.c.}, \quad (\text{I } 4) \\ & \frac{\Delta_{so}}{\omega - \lambda_4} \left[\frac{1}{i\Gamma(\Delta_{so} + i\Gamma)} + \frac{1}{(2\mathcal{E} - 5\beta/2)^2} \right] + \text{c.c.} \end{aligned}$$

Since $\mathcal{E} \gg \Delta_{so}, \Gamma$ the second terms in the brackets are very much smaller than the first terms. Furthermore, we observe that they have opposite signs in the λ_1 and λ_2 terms (resonant terms) and therefore will give an additional cancellation after the integrals of λ_1 and λ_2 [see (17)] have been summed. The large coefficients $1/(i\Gamma)(\Delta_{so} \pm i\Gamma)$ in the λ_1 and λ_2 terms have the opposite sign to those, respectively, in λ_4 and λ_3 terms, hence there will also be cancellation between the (λ_1, λ_2) terms and the (λ_4, λ_3) terms but here one is confronted with the $\bar{\text{Ei}}$ function again, but this time with both positive and negative arguments. Thus, although the effect of the nonresonant terms appears to involve complicated cancellations it may be shown that they introduce terms of order $(\Delta_{so}/\mathcal{E})^2$ times the resonant terms. This general result also applies for the Taylor-series-expansion approach. One can show that the power-law Raman process due to the $1 S-T_2$ levels contains contributions proportional to both $(\Delta_{so}^2/\mathcal{E}^2)T^7$ and $(\Delta_{so}^2/\mathcal{E}^4)T^9$ for $nkT \ll \mathcal{E}$. The T^9 temperature dependence would arise from a Van Vleck-type cancellation.¹⁹

APPENDIX II. HIGHER-ORDER TERMS IN TAYLOR EXPANSION

To check the effect of higher-order terms in the transition probability in (24) we shall explicitly calculate the second-order term. Although the choice of the symmetrical limits about the mean of the energies $\mathcal{E} - 2\beta$ and $\mathcal{E} + \beta$ would appear to make the odd terms small they are still not completely negligible compared to the higher-order even terms in (24). The integrals we need for the second-order term can be evaluated by direct integration and are

$$\int_{-(a-3\beta/2)}^{a+3\beta/2} \frac{x^2 dx}{x^2 + (\Gamma/2)^2} = \int_{-(a+3\beta/2)}^{a-3\beta/2} \frac{x^2 dx}{x^2 + (\Gamma/2)^2} = I(a). \quad (\text{II } 1)$$

$$\left[\int_{-a}^a \frac{x^2 dx}{(x+3\beta/2-i\Gamma/2)(x-3\beta/2+i\Gamma/2)} + \text{c.c.} \right] = 2I(a) + 3\beta \ln \left[\frac{(a-3\beta/2)^2 + (\Gamma/2)^2}{(a+3\beta/2)^2 + (\Gamma/2)^2} \right]^{1/2},$$

where

$$I(a) = 2a - \frac{\Gamma}{2} \left[\pi - \frac{\Gamma}{a} \left(1 + \left(\frac{3\beta}{2a} \right)^2 \right) + O\left(\frac{\Gamma}{a} \right)^3 + \dots \right]. \quad (\text{II } 2)$$

It is observed that the integrals in (II1) are the same except for the extra \ln term which means there will be substantial cancellation when the second-order terms in (24) are added together. For $a \gg \Gamma, \beta$ the \ln term may be expanded to yield

$$3\beta \ln \left[\frac{(a-3\beta/2)^2 + (\Gamma/2)^2}{(a+3\beta/2)^2 + (\Gamma/2)^2} \right]^{1/2} \simeq - \left(\frac{\Delta_{so}}{a} \right)^2 a. \quad (\text{II } 3)$$

The second-order contribution to the transition probability becomes

$$\begin{aligned}
 W_{A_1 \uparrow \rightarrow A_1 \downarrow}^2 = & \frac{2\pi (a^+ b^+ + a^- b^-)^2 e^{-\varepsilon/kT}}{\hbar^2} \frac{1}{2} \left\{ I(a) \left[\left[\frac{d^2}{dx^2} (G(\varepsilon - 2\beta + x) e^{-x/kT}) \right]_{x=0} e^{2\beta/kT} \right. \right. \\
 & + \left. \left[\frac{d^2}{dx^2} (G(\varepsilon + \beta + x) e^{-x/kT}) \right]_{x=0} e^{-\beta/kT} - 2 \left[\frac{d^2}{dx^2} (G(\varepsilon - \beta/2 + x) e^{-x/kT}) \right]_{x=0} e^{(\beta/2kT)} \right. \\
 & \left. \left. + 2a \left(\frac{\Delta_{so}}{a} \right)^2 \left[\frac{d^2}{dx^2} (G(\varepsilon - \beta/2 + x) e^{-x/kT}) \right]_{x=0} e^{\beta/2kT} \right\}. \quad (\text{II } 4)
 \end{aligned}$$

The terms inside the square bracket times $I(a)$ are first evaluated at $x=0$ and are then expanded to second-order terms in $(\beta/\varepsilon)^2$ and $(\beta/kT)^2$. One finds that the zeroth-order and the first-order terms in β identically vanish leaving only second-order and higher-order terms. One also sees that the remaining term in (II4) will be comparable or smaller than the second-order term in the expansion for large enough a . Neglecting this term the result is

$$W_{A_1 \uparrow \rightarrow A_1 \downarrow}^2 = \frac{2\pi (a^+ b^+ + a^- b^-)^2 e^{-\varepsilon/kT}}{\hbar^2} \frac{\Delta_{so}^2}{4} I(a) \left[G^{\text{IV}}(\varepsilon) - 4 \frac{G^{\text{III}}(\varepsilon)}{kT} + 6 \frac{G^{\text{II}}(\varepsilon)}{(kT)^2} - 4 \frac{G^{\text{I}}(\varepsilon)}{(kT)^3} + \frac{G(\varepsilon)}{(kT)^4} \right]. \quad (\text{II } 5)$$

Using $G(\omega) = A\omega^n$ we can readily compare this to (22) and we find

$$\begin{aligned}
 W_{A_1 \uparrow \rightarrow A_1 \downarrow}^2 = & W_{A_1 \uparrow \rightarrow A_1 \downarrow}^0 \left(\frac{1}{2\pi} \right) \frac{I(a)}{16\Gamma} \frac{\Gamma^2(\Delta_{so}^2 + \Gamma^2)}{(kT)^4} \left[n(n-1)(n-2)(n-3) \left(\frac{kT}{\varepsilon} \right)^4 - 4n(n-1)(n-2) \left(\frac{kT}{\varepsilon} \right)^3 \right. \\
 & \left. + 6n(n-1) \left(\frac{kT}{\varepsilon} \right)^2 - 4n \left(\frac{kT}{\varepsilon} \right) + 1 \right]. \quad (\text{II } 6)
 \end{aligned}$$

The factor in the square brackets is a factor less than unity for typical values of kT/ε in the Orbach-process temperature region. For $kT/\varepsilon = \frac{1}{6}$ the bracket is $1/18$ while for $kT/\varepsilon = 1/12$ the bracket is $-1/92$ if we set $n=6$. Consequently the second-order term will clearly be negligible in comparison with the zeroth-order term as long as Γ is enough less than kT . This is simply a statement that the Orbach-resonance part of the Raman integrand must be substantially narrower than the thermal ($\omega_{I\text{max}} \sim nkT$) part of the integrand which gives the power-law term and this is a very reasonable condition for the expansion in (23) to be valid.