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Double-Quantum Transitions in a Three-Level Electronic Spin System

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A general formula describing the relaxation by double-quantum transitions in a three-level electronic spin system is given. The results are interpreted in terms of a parameter $\alpha=\Theta_c/\Theta_D$, of contact between the excited spin energy level at temperature Θ_c and the phonon spectrum of Debye temperature Θ_D. The usual Raman and Orbach processes for Kramers and non-Kramers salts are derived.

1. INTRODUCTION

USUAL double-quantum paramagnetic spin-lattice relaxation is described as a function of the absolute temperature T, by a Raman $T_1 \propto T^{-7}$ law for a non-Kramers salt, by a $T_1 \propto T^{-9}$ law for a Kramers salt, and also by an Orbach exponential law $T_1 \propto \exp(\Delta_c/kT)$, where Δ_c is the energy of the excited $|c\rangle$ level.

We remind the reader that the rate equations for a three-energy-level spin system $|a\rangle$, $|b\rangle$, and $|c\rangle$ as shown as in Fig. 1 lead to the equation

$$d(n_a-n_b)/dt=2p_{ba}n_b-2p_{ab}n_a +(p_{ca}-p_{cb})n_c+p_{bc}n_b-p_{ac}n_a\,,$$

where n_i is the instantaneous population value of level $|i\rangle$ and p_{ij} is the relaxation transition probability between levels $|i\rangle$ and $|j\rangle$.

In the general case, where $\delta_{ab}\ll kT<\Delta_c$ and $p_{bc}\sim p_{ac}$, one obtains[1]

$$d(n_a-n_b)/dt=p_{bc}(n_b-n_a)\,,$$

so that the spin-lattice relaxation time for this special three-level system reduces to $T_1^{-1}\sim p_{bc}$.

Orbach[2] considers one-phonon direct processes for transitions with level $|c\rangle$, so that

$$T_1^{-1}\sim p_{bc}\sim \frac{\omega_{bc}^3}{\exp(\hbar\omega_{bc}/kT)-1}\sim\left(\frac{\Delta_c}{\hbar}\right)^3\exp\left(-\frac{\Delta_c}{kT}\right).$$

Only Δ_c energy phonons occur in this calculation and it seems that an important part of the phonon spectrum is neglected. In Sec. 2, we undertake the calculation of the spin-lattice relaxation time T_1, taking the whole phonon spectrum into account.

2. DOUBLE-QUANTUM TRANSITIONS IN A THREE-LEVEL SYSTEM

The number of phonons of angular frequency ω in the sample at absolute temperature T is proportional to $\omega^2/[\exp(\hbar\omega/kT)-1]$.

Among the two-phonon processes induced by the second-order V_2e^2 term of the crystalline potential expansion, we now consider not only the Raman process, that is the absorption of a phonon ω_1 and the emission of a phonon ω_2 such as $\omega_1-\omega_2=\Delta_c/\hbar$, but also the absorption or emission of two phonons ω_1 and $\omega_2<\Delta_c/\hbar$ such as $\omega_1+\omega_2=\Delta_c/\hbar$.

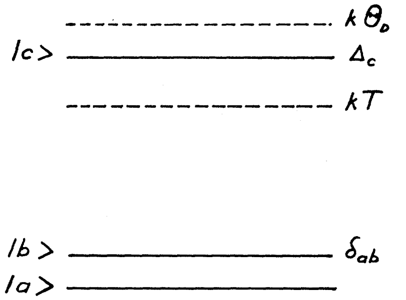

FIG. 1. Three-level spin system: $\delta_{ab}\ll kT<\Delta_c$.

The phonons ω_1 and ω_2 having occupation numbers N_1 and N_2, respectively, we have to consider for an absorption $\omega_1+\omega_2=\Delta_c/\hbar$, matrix elements such as $|\langle c, N_1-1, N_2-1|V_2e^2|b, N_1, N_2>|^2$. If ρ is the crystal density and v the phonon velocity, one obtains a probability equal to

$$\frac{9}{8\pi^3\rho^2v^{10}}|\langle b|V_2|c\rangle|^2\int_0^{\Delta_c/\hbar}\frac{\omega_1^3(\Delta_c/\hbar-\omega_1)^3}{[\exp(\hbar\omega_1/kT)-1]\{\exp[(\Delta_c-\hbar\omega_1)/kT]-1\}}d\omega_1.$$

If now a phonon $\omega_1>\Delta_c/\hbar$ is absorbed and the phonon ω_2 emitted, the matrix element becomes $|\langle c, N_1-1, N_2+1|V_2e^2|b, N_1, N_2\rangle|^2$ so that if the Debye frequency is Ω such as $\Delta_c/\hbar<\omega_1<\Omega$, the rate for this process is equal to

$$\frac{9}{8\pi^3\rho^2v^{10}}|\langle b|V_2|c\rangle|^2\int_{\Delta_c/\hbar}^{\Omega}\frac{\exp[(\hbar\omega_1-\Delta_c)/kT]}{[\exp(\hbar\omega_1/kT)-1]\{\exp[(\hbar\omega_1-\Delta_c)/kT]-1\}}\omega_1^3\left(\omega_1-\frac{\Delta_c}{\hbar}\right)^3d\omega_1.$$

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[1] C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **77**, 261 (1961).
[2] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

Taking account of the two double-quantum processes, one finally finds that

$$\frac{1}{T_1}\sim\frac{9}{8\pi^3\rho^2v^{10}}|\langle b|V_2|c\rangle|^2\int_0^{\Omega}\frac{\exp[(\hbar\omega_1-\Delta_c)/kT]}{[\exp(\hbar\omega_1/kT)-1]\{\exp[(\hbar\omega_1-\Delta_c)/kT]-1\}}\omega_1^3\left(\omega_1-\frac{\Delta_c}{\hbar}\right)^3d\omega_1. \tag{1}$$

Let

$$\hbar\omega_1/kT=x\,,\quad 0<x<\hbar\Omega/kT=\Theta_D/T\,,\quad\text{and}\quad \Delta_c=k\Theta_c;$$

the integral in (1) can then be written

$$J_7\left(\frac{\Theta_D}{T}\right)=e^{-\Theta_c/T}\left(\frac{kT}{\hbar}\right)^7\times\int_0^{\Theta_D/T}\frac{e^xx^3(x-\Theta_c/T)^3}{(e^x-1)(e^{x-\Theta_c/T}-1)}dx. \tag{2}$$

So, one sees that an Orbach exponential term is multiplied by a Raman T^{-7} relaxation expression. Finding the domain of validity of each law requires the calculation of the integral in (2). We therefore define a parameter $\alpha=x_c/x_D=\Theta_c/\Theta_D$ of contact between the spin system characterized by $x_c=\Theta_c/T$ and the phonon spectrum characterized by $x_D=\Theta_D/T$.

The preceding integral proportional to

$$I_7(x_D)=\int_0^{x_D}\frac{e^{-\alpha x_D}}{x_D{}^7}\frac{e^xx^3(x-\alpha x_D)^3}{(e^x-1)(e^{x-\alpha x_D}-1)}dx$$

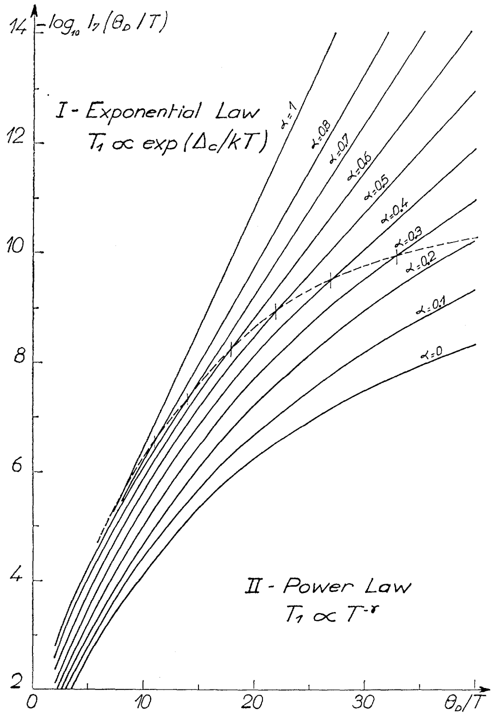

FIG. 2. Plot of $\log_{10}AT_1$ as a function of Θ_D/T, for non-Kramers salts.

thus gives the variation law of T_1^{-1} as a function of temperature.

The results obtained for different values of the parameter α $(0\leqslant\alpha\leqslant1)$ are given in Figs. 2 and 3. The integral is calculated as a function of x_D, x_D varying from 0 to 40. Figure 2 shows the variations of $\log_{10}AT_1$, where A is an arbitrary constant, as a function of Θ_D/T; Fig. 3 shows the same variations as a function of $\log_{10}(\Theta_D/T)$. The vertical marks on both series of curves give the lower limits of pure exponential laws.

In both figures the dashed line separates the x-y plane into the following two regions: the upper one noted (I) corresponding to a true exponential variation of T_1, and the lower one noted (II) corresponding to a rather power variational law of T_1 with slopes of the order of 5–9.

For $\alpha=0$, one finds the classical relaxation integral, giving the Raman T^{-7} law, which has been studied elsewhere[1,3,4]; (1) then reduces to

$$\left(\frac{1}{T_1}\right)_{\alpha=0}=p_{\alpha=0}=\frac{9}{8\pi^3\rho^2v^{10}}|\langle b|V_2|c\rangle|^2\left(\frac{k\Theta_D}{\hbar}\right)^7 732\left(\frac{T}{\Theta_D}\right)^7.$$

In the more general case, that is, for $\alpha\neq0$, (1) can be written

$$\left(\frac{1}{T_1}\right)_{\alpha}=p_\alpha=\frac{9}{8\pi^3\rho^2v^{10}}|\langle b|V_2|c\rangle|^2\left(\frac{k\Theta_D}{\hbar}\right)^7K_7e^{-\Theta_c/T},$$

where $K_7=I_7e^{\alpha x_D}$ with the particular value $K_7=7.17\times10^{-3}$ for $\alpha=1$.

To evaluate the importance of this additional contribution to $1/T_1$, it is necessary to estimate the magnitude of the two-phonon contributions of probability p_α as compared to the one-phonon contributions of probability p_0. The corresponding one-phonon relaxation process will be described by the usual expression[2]

$$\frac{1}{T_1}=p_0=\frac{3}{2\pi\rho v^5\hbar^4}|\langle b|V_1|c\rangle|^2\Delta_c{}^3e^{-\Delta_c/kT}.$$

Then

$$\frac{p_\alpha}{p_0}=\frac{3k^4}{4\pi^2\rho v^5\hbar^3}\frac{|\langle b|V_2|c\rangle|^2}{|\langle b|V_1|c\rangle|^2}K_7\frac{\Theta_D{}^4}{\alpha^3}.$$

With the approximate following values $\rho=2\times10^3$ kg/m^3, $v=2\times10^3$ m/sec, $k=1.4\times10^{-23}$ J/deg, and $\hbar=10^{-34}$

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[3] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[4] R. Le Naour, Compt. Rend. **B266**, 1125 (1968).

J sec, one finds that

$$\frac{p_\alpha}{p_0} \sim \frac{K_7}{2\times 10^{10}} \frac{|\langle b|V_2|c\rangle|^2}{|\langle b|V_1|c\rangle|^2} \frac{\Theta_D{}^4}{\alpha^3}.$$

In general, the double-quantum process should be more important at the highest of temperatures. It overcrosses the one-phonon contribution for lower α values. We calculate p_α/p_0 for two typical Debye temperatures. For $\Theta_D \sim 60°\text{K}$,[5] $\langle b|V_1|c\rangle \sim 21\ \text{cm}^{-1}$ and $\alpha=0.5$, $p_\alpha > p_0$ for $T > 5°\text{K}$. For $\Theta_D \sim 750°\text{K}$,[6] $\langle b|V_1|c\rangle \sim 105\ \text{cm}^{-1}$ and $\alpha = 0.2$, $p_\alpha > p_0$ for $T > 150°\text{K}$.

It is interesting to investigate what happens at the limiting value $\Theta_D \gg \Theta_c$, that is, $\alpha \to 0$. From the general expressions of $p_{\alpha=0}$ and p_0, one finds that

$$\frac{p_{\alpha=0}}{p_0} = \frac{3\times 732 k^4}{4\pi^2 \rho v^5 \hbar^3} \frac{|\langle b|V_2|c\rangle|^2}{|\langle b|V_1|c\rangle|^2} \Theta_c{}^4 \left(\frac{T}{\Theta_c}\right)^7 e^{\Theta_c/T},$$

so that with the same preceding values to which we add those of $\Theta_c \sim 300°\text{K}$ and $\langle b|V_1|c\rangle \sim \langle b|V_2|c\rangle$, this reduces to

$$p_{\alpha=0}/p_0 \simeq 3\times 10^{-8} \Theta_c{}^4 x_c{}^{-7} e^{x_c}.$$

The double-quantum term will then be more important at the very lowest and highest of temperatures; this corresponds here to $T < 30°\text{K}$ and $T > 80°\text{K}$.

Of course, at still lower temperatures the relaxation between levels $|a\rangle$ and $|b\rangle$ will be described by the direct process

$$\frac{1}{T_1} = p_d = \frac{3}{\pi \hbar^4 \rho v^5} |\langle a|V_1|b\rangle|^2 \Delta_b{}^2 kT,$$

so that

$$\frac{p_d}{p_{\alpha=0}} = \frac{8\pi^2 \rho v^5}{3\times 732} \frac{\hbar^3}{k^6} \frac{|\langle a|V_1|b\rangle|^2}{|\langle b|V_2|c\rangle|^2} \Delta_b{}^2 T^{-6}.$$

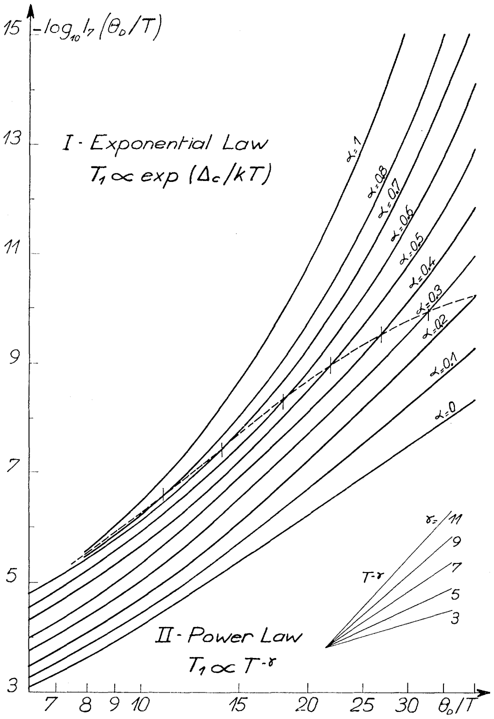

FIG. 3. Plot of $\log_{10} AT_1$ as a function of $\log_{10}\Theta_D/T$, for non-Kramers salts.

With the additional values $\langle a|V_1|b\rangle \sim \Delta_b \sim 1\ \text{cm}^{-1}$ and $\langle b|V_2|c\rangle \sim 100\ \text{cm}^{-1}$, one finds that the direct one-phonon process will be dominant for $T < 4°\text{K}$.

The preceding results have been obtained by considering a two-phonon relaxation process induced by the second-order V_2e^2 term of the crystalline potential expansion.

If V_1e is the first-order term of the same potential expansion, double-quantum transitions can be introduced by second-order time-dependent perturbation theory, and so involves V_1e taken twice. Matrix elements are then written

$$\sum_t \frac{\langle c, N_1-1, N_2-1|V_1'e'|t, N_1-1, N_2\rangle\langle t, N_1-1, N_2|V_1e|b, N_1, N_2\rangle}{-(\Delta_t - \hbar\omega_1)},$$

where $|t\rangle$ is an intermediate state at energy Δ_t above the fundamental level $|a\rangle$.

An absorption $\omega_1+\omega_2=\Delta_c/\hbar$ is described by the probability

$$\frac{2\pi}{\hbar} \frac{\hbar^2}{4M^2v^4} \int_0^{\Delta_c/\hbar} \left| \sum_t \frac{\langle c|V_1'|t\rangle\langle t|V_1|b\rangle}{\hbar\omega_1 - \Delta_t} + \sum_t \frac{\langle c|V_1|t\rangle\langle t|V_1'|b\rangle}{\hbar\omega_2 - \Delta_t} \right|^2 N_1 N_2\, \omega_1\omega_2 \frac{g(\omega_2)}{\hbar} g(\omega_1)\, d\omega_1,$$

where M is the crystal's mass, $g(\omega)$ the density function of phonon modes, and $\hbar\omega_2 - \Delta_t = \Delta_c - \hbar\omega_1 - \Delta_t$.

If now the phonon $\omega_1 > \Delta_c/\hbar$ is absorbed, and the phonon ω_2 emitted, the rate becomes

$$\frac{2\pi}{\hbar} \frac{\hbar^2}{4M^2v^4} \int_{\Delta_c/\hbar}^{\Omega} \left| \sum_t \frac{\langle c|V_1'|t\rangle\langle t|V_1|b\rangle}{\hbar\omega_1 - \Delta_t} + \sum_t \frac{\langle c|V_1|t\rangle\langle t|V_1'|b\rangle}{-\hbar\omega_2 - \Delta_t} \right|^2 N_1(N_2+1)\omega_1\omega_2 \frac{g(\omega_2)}{\hbar} g(\omega_1)\, d\omega_1,$$

where $-\hbar\omega_2 - \Delta_t = \Delta_c - \hbar\omega_1 - \Delta_t$.

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[5] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

[6] J. G. Castle, D. W. Feldman, and P. G. Klemens, *Advances in Quantum Electronics* (Columbia University Press, New York, 1961), p. 414.

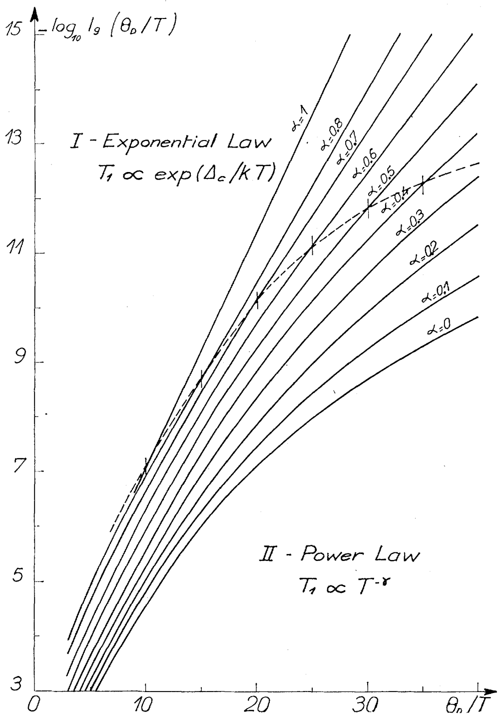

FIG. 4. Plot of $\log_{10} AT_1$ as a function of Θ_D/T, for Kramers salts.

Taking account of the two double-quantum processes, we find that

$$p_{bc}=\frac{9}{8\pi^3\rho^2v^{10}}\int_0^\Omega\left|\sum_t\frac{\langle c|V_1'|t\rangle\langle t|V_1|b\rangle}{\hbar\omega_1-\Delta_t}+\sum_t\frac{\langle c|V_1|t\rangle\langle t|V_1'|b\rangle}{\Delta_c-\hbar\omega_1-\Delta_t}\right|^2\times\frac{\exp[(\hbar\omega_1-\Delta_c)/kT]}{[\exp(\hbar\omega_1/kT)-1]\{\exp[(\hbar\omega_1-\Delta_c)/kT]-1\}}\times\omega_1^3\left(\omega_1-\frac{\Delta_c}{\hbar}\right)^3d\omega_1. \quad (3)$$

In the case $\hbar\omega_1 \ll \Delta_t$, one obtains for non-Kramers salts the same temperature dependence as given by Eq. (1).

For Kramers salts, however, levels $|b\rangle$, $|c\rangle$, and $|t\rangle$ are time-reversed doublets so that important symmetry properties[2] of matrix elements such as $\langle\frac{1}{2}c|V_1'|\frac{1}{2}t\rangle\langle\frac{1}{2}t|V_1|\frac{1}{2}b\rangle$ must be considered.

Finally, for $\hbar\omega_1<\Delta_t$, which is the case if $k\Theta_D<\Delta_t$, one finds by a development of the integrand, a relaxation rate proportional to

$$\int_0^\Omega\frac{\exp[(\hbar\omega_1-\Delta_c)/kT]}{[\exp(\hbar\omega_1/kT)-1]\{\exp[(\hbar\omega_1-\Delta_c)/kT]-1\}}\times\omega_1^5\left(\omega_1-\frac{\Delta_c}{\hbar}\right)^3d\omega_1.$$

With our preceding notations, this expression can be written

$$J_9\left(\frac{\Theta_D}{T}\right)=e^{-\Theta_c/T}\left(\frac{kT}{\hbar}\right)^9\times\int_0^{\Theta_D/T}\frac{e^xx^5(x-\Theta_c/T)^3}{(e^x-1)(e^{x-\Theta_c/T}-1)}dx. \quad (4)$$

Figures 4 and 5 show the variations, for $0\leqslant\alpha\leqslant1$, of the integral

$$I_9(x_D)=\int_0^{x_D}\frac{e^{-\alpha x_D}}{x_D^9}\frac{e^xx^5(x-\alpha x_D)^3}{(e^x-1)(e^{x-\alpha x_D}-1)}dx,$$

which gives the T_1^{-1} relaxation law as a function of temperature.

For $\alpha=0$, one finds the usual Raman relaxation integral[4] showing a T^{-9} dependence for Kramers salts.

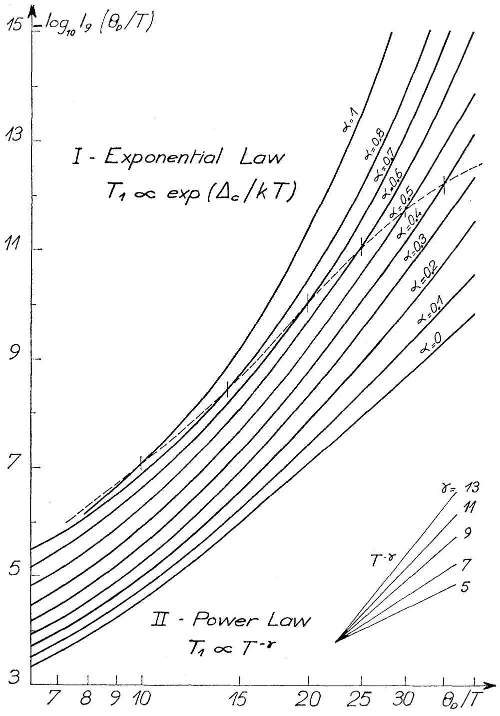

FIG. 5. Plot of $\log_{10} AT_1$ as a function of $\log_{10}\Theta_D/T$, for Kramers salts.

For $\alpha \neq 0$, a Raman process is in competition with the Orbach exponential process. As before, in Figs. 4 and 5, the vertical marks give the lower limits of pure exponential laws.

In the case of rare-earth ethylsulphates ($\Theta_D \sim 60°$K), for measurements between 1.5 and 4°K, the interesting region of our curves is in the $15 < \Theta_D/T < 40$ range. For a paramagnetic ion in MgO ($\Theta_D \sim 820°$), the transitional temperature between the two processes is, for $\alpha = 0.5$, about 40°K.

3. CONCLUSION

The study of double-quantum spin-lattice relaxation in a particular three-level system, leads to a relaxation law of the form

$$T_1^{-1} \sim K I_n\left(\frac{\Theta_D}{T}\right) = K e^{-\alpha\Theta_D/T}\left(\frac{T}{\Theta_D}\right)^n \times \int_0^{\Theta_D/T} \frac{e^x x^{n-4}(x-\alpha\Theta_D/T)^3}{(e^x-1)(e^{x-\alpha\Theta_D/T}-1)} dx\,,$$

where K is a constant, $n=7$ for non-Kramers salts, or $n=9$ for Kramers salts, and where the parameter $\alpha = \Theta_c/\Theta_D$ describes the contact between the studied three-level system and the phonon spectrum characterized by its Debye temperature.

Calculations show that the ordinary Raman and Orbach processes are derived as particular cases.

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Stopping Power of Matter for Deuterons at Extreme Relativistic Energies[*]

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The stopping power of matter for deuterons at extreme relativistic energies ($\lesssim$2000 GeV) has been calculated. The structure of this particle and its spin are taken into account explicitly. It is found that the ultrarelativistic effects reduce the stopping power (as predicted by the relativistic formula) by 8% at the highest energies considered. These effects are analyzed numerically and compared with the estimated density correction. A stopping-power table for deuterons in aluminum is computed.

THE stopping power of matter for protons and muons (spin $\frac{1}{2}$) at extreme relativistic energies was calculated[1] by taking into account the particles's spin, anomalous magnetic moment, and distributions of charge and magnetic moment (particle form factors). In this paper we extend this work to include the deuteron (spin 1).

The differential cross section for scattering of an electron (charge $-e$, rest mass m, and velocity v) at an angle θ from a spinless point particle (charge ze and rest mass M_d), initially at rest, is[2]

$$\left(\frac{d\sigma}{d\Omega}\right)_0 = \left(\frac{ze^2}{2\gamma m v^2}\right)^2 \frac{\cos^2(\frac{1}{2}\theta)}{\sin^4(\frac{1}{2}\theta)} \left(1 + \frac{2\gamma m}{M_d}\sin^2\tfrac{1}{2}\theta\right)^{-1}, \quad (1)$$

where $\gamma = (1-\beta^2)^{-1/2}$, $\beta = v/c$ being the speed of the electron in terms of the speed of light c. Gourdin[3] derived an expression for the scattering of electrons from deuterons by using a nonrelativistic wave function for the deuteron. We write[4,5]

$$\frac{d\sigma}{d\Omega} = \left(\frac{d\sigma}{d\Omega}\right)_0 \left[\frac{G_{Ed}^2(q^2)}{1+\tau} + \frac{8\tau^2}{9}\frac{G_{Qd}^2(q^2)}{1+\tau} + \frac{2\tau}{3} G_{Md}^2(q^2)\left(\frac{1}{1+\tau} + 2\tan^2\tfrac{1}{2}\theta\right)\right], \quad (2)$$

where $\hbar q$ is the magnitude of the change in the electron's (=deuteron's) energy-momentum four-vector; $\tau = \hbar^2 q^2/4M_d^2c^2$, M_d being the mass of the deuteron; and

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[2] N. F. Mott and H. S. W. Massey, *Theory of Atomic Collisions* (Oxford University Press, Oxford, 1965), 3rd ed.

[3] M. Gourdin, Nuovo Cimento **28**, 533 (1963). Also see *Diffusion des Électrons de Haute Énergie*, (Masson Cie, Paris, 1966).

[4] R. Wilson, in *Particle Interactions at High Energies*, edited by T. W. Priest and L. L. J. Vick (Oliver and Boyd, London, 1967). The factor τ^2 multiplying G_{Md} in Eq. (35) of this paper should be replaced by τ and the coefficient $-3/18$ in Eq. (45) by $\frac{3}{4}$.

[5] J. E. Elias, J. I. Friedman, G. C. Hartmann, H. W. Kendall, P. N. Kirk, M. R. Sogard, L. P. Van Speybroeck, and J. K. de Pagter, Phys. Rev. **177**, 2075 (1969). As seen from Fig. 7 of this reference, some error is introduced at large values of q by use of a nonrelativistic deuteron wave function. In view of the relatively small magnitude of the structural effects, however, this should not markedly alter the numerical results.