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Spin Relaxation via Modulation of the Orbital Energy

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In contrast to previous treatments, we present a spin-lattice-relaxation theory according to which the crystalline-modulated potential is considered as a quasistationary perturbation which entails modulation of orbitals and modulation of energy. One of these effects has been studied previously. We study here the second of them, namely, spin relaxation via modulation of the orbital energy.

In previous papers[1-3] it has been shown that when spin-lattice relaxation occurs, the transitions are induced between wave functions whose orbital part follows adiabatically the displacements of the crystalline complex. The correct way to study spin-lattice relaxation is thus to consider the crystalline-modulated potential as a quasistationary perturbation, whose effect is to entail polarization and rotation of the orbitals. These act secondarily on the spin system, through spin-orbit interaction.

We now consider another adiabatic relaxation mechanism by which the crystalline-modulated potential does not act directly on the spin system but indirectly, namely, relaxation via modulation of orbital energy.

The total Hamiltonian for the paramagnetic system coupled to the rigid lattice can be written as

$$\mathcal{H}=\mathcal{H}_0+2\beta\,\vec{\mathrm{S}}\cdot\vec{\mathrm{H}}+\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}+\lambda\,\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}+V_c+\mathcal{H}_L, \quad (1)$$

where $\mathcal{H}_0$ is the Hamiltonian for the free ion, V_c is the crystalline potential, which can be expanded as a function of the deformations of the crystalline complex

$$V_c=V_c^{(0)}+V_c^{(1)}\epsilon+V_c^{(2)}\epsilon^2+\cdots .$$

$\mathcal{H}_L$ is the Hamiltonian of the lattice vibrations $\mathcal{H}_L=\sum_p(a_p^+a_p+\frac{1}{2})\hbar\omega$, and $\vec{\mathrm{H}}$ is the external magnetic field.

We call φ_0 and φ_n the eigenfunctions of $\mathcal{H}_0+V_c^{(0)}$, and E_0 and E_n the energies associated with these functions. As shown previously,[1-3] $V_c^{(1)}\epsilon$ for the direct process (and $V_c^{(2)}\epsilon^2$ for the Raman process) can be considered as a slow-varying perturbation, so that the energies associated with $\mathcal{H}_0+V_c^{(0)}+V_c^{(1)}\epsilon$ are equal, to first order, to the following expressions:

$$\epsilon_0=E_0+\langle\varphi_0|V_c^{(1)}\epsilon|\varphi_0\rangle,$$

$$\epsilon_n=E_n+\langle\varphi_n|V_c^{(1)}\epsilon|\varphi_n\rangle .$$

If we limit our study to the spin states associated with the ground orbital state, we can use an effective-Hamiltonian formalism. As usual,[4] the effective Hamiltonian can be written as[5]

$$\mathcal{H}_{\mathrm{eff}}=\sum_{n\sigma}\frac{\mathcal{H}_{\mathrm{pert}}|\varphi_n\sigma\rangle\langle\varphi_n\sigma|\mathcal{H}_{\mathrm{pert}}}{\epsilon_0-\epsilon_n}+2\beta\,\vec{\mathrm{S}}\cdot\vec{\mathrm{H}}, \quad (2)$$

where $\mathcal{H}_{\mathrm{pert}}=\lambda\,\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}+\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}$.

Knowing the ability of $V_c^{(1)}\epsilon$ to induce phonon transitions, we can part $\mathcal{H}_{\mathrm{eff}}$ into a sum of two terms, one being static and the other modulated. Since the perturbation energies are small with respect to E_0 and E_n, we get

$$\mathcal{H}_{\mathrm{eff}}=\sum_{n\sigma}\left\{\frac{\mathcal{H}_{\mathrm{pert}}|\varphi_n\sigma\rangle\langle\varphi_n\sigma|\mathcal{H}_{\mathrm{pert}}}{E_0-E_n}\right\}$$

$$\times\left(1-\frac{\langle\varphi_0|V_c^{(1)}\epsilon|\varphi_0\rangle-\langle\varphi_n|V_c^{(1)}\epsilon|\varphi_n\rangle}{E_0-E_n}\right)+2\beta\vec{\mathrm{S}}\cdot\vec{\mathrm{H}} .$$

The term

$$\mathcal{H}_{\mathrm{eff}}^0=\sum_{n\sigma}\frac{\mathcal{H}_{\mathrm{pert}}|\varphi_n\sigma\rangle\langle\varphi_n\sigma|\mathcal{H}_{\mathrm{pert}}}{E_0-E_n}+2\beta\vec{\mathrm{S}}\cdot\vec{\mathrm{H}} \quad (3)$$

is the static effective Hamiltonian, while the term depending on ϵ is the dynamic one. If we put ϵ outside of the summation this latter one becomes

$$\tilde{\mathcal{H}}_{\mathrm{eff}}$$

$$=-\epsilon\sum_{n\sigma}\frac{(V_c^{(1)}{}_{00}-V_c^{(1)}{}_{nn})\mathcal{H}_{\mathrm{pert}}|\varphi_n\sigma\rangle\langle\varphi_n\sigma|\mathcal{H}_{\mathrm{pert}}}{(E_0-E_n)^2} . \quad (4)$$

The total effective Hamiltonian can thus be written as

$$\mathcal{H}^0_{\mathrm{eff}} + \tilde{\mathcal{H}}_{\mathrm{eff}} + \mathcal{H}_L \ .$$

We call $\varphi_0 \sigma'' N$ and $\varphi_0 \sigma' (N+1)$ two eigenstates of $\mathcal{H}^0_{\mathrm{eff}} + \mathcal{H}_L$ obeying the energy-conservation equation, $E_{\sigma''} - E_{\sigma'} = E_{N+1} - E_N$. The spin-relaxation probability through modulation of the orbital energy can then be written as follows[6]:

$$\begin{aligned} & W_{\sigma'' N \to \sigma' (N+1)} \\ & = (2\pi/\hbar) \left| \langle \varphi_0 \sigma'' N | \mathcal{H}_{\mathrm{eff}} | \varphi_0 \sigma' (N+1) \rangle \right|^2 \rho(E) \\ & = (2\pi/\hbar) \left| \sum_n \left\{ \sum_\sigma \langle \varphi_0 \sigma'' | \mathcal{H}_{\mathrm{pert}} | \varphi_n \sigma \rangle \right. \right. \\ & \quad \times \langle \varphi_n \sigma | \mathcal{H}_{\mathrm{pert}} | \varphi_0 \sigma' \rangle \\ & \quad \left. \left. \times \frac{\langle N | (V_c^{(1)}{}_{00} - V_c^{(1)}{}_{nn}) \epsilon | N+1 \rangle}{(E_0 - E_n)^2} \right\} \right|^2 \rho(E). \qquad (5) \end{aligned}$$

This probability being calculated with the unperturbed wave functions of the Hamiltonian $\mathcal{H}_0 + V_c^{(0)} + 2\beta \vec{S} \cdot \vec{H} + \mathcal{H}_L$, the only effect of $V_c^{(1)} \epsilon$ results in the occurrence of diagonal terms $V_c^{(1)}{}_{00}$ and $V_c^{(1)}{}_{nn}$ in expression (5). This effect should contribute also also, and be added to that studied in our previous paper.[3] There, $V_c^{(1)} \epsilon$ was considered as a perturbation for the wave functions between which the matrix elements have to be taken.

Note added in proof. In Ref. 3, formula (21), the diagonal terms $V_c^{(1)}{}_{xx}$ and $V_c^{(1)}{}_{zz}$ had been neglected. The occurrence of these terms would not have changed the conclusions of the theory, but only the value of $\tilde{\theta}$ which would have been

$$\begin{aligned} \tilde{\theta} = & (V_c^{(1)} \epsilon_{xz} / \Delta) \cos 2\theta_m \\ & + [(V_c^{(1)} \epsilon_{zz} - V_c^{(1)} \epsilon_{xx}) / \Delta] \sin 2\theta_m \ . \end{aligned}$$

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[5] We shall omit here, the modulation of orbitals which has been studied in Ref. 3.

[6] In a general study, it would be necessary to take account simultaneously of modulation of orbitals and modulation of energy, and crossed terms would contribute also.