ytterbium is dipolar in nature, this large ratio of B/A is due to the large ratio of $g_\perp/g_\parallel$ for these crystals. We note that the S band spectra of all these crystals, including $CaWO_4$, would exhibit the unusual behavior similar to that described above. However, the K band spectra would exhibit the normal behavior observed for Yb^{3+} in $CaWO_4$ since γ would then be greater than γ_c.

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Adiabatic Quantum Theory of Spin-Lattice Relaxation

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A theory of spin-lattice relaxation is presented in which the modulated crystalline potential does not act directly, but entails modulation of orientation and polarization of the orbitals. These factors are responsible for a modulation of the effective magnetic field acting on the electron spin, which supplies the spin transitions. Three consequences result from this formulation: (a) The spin Zeeman term does not play its traditional role in the relaxation process, the reason for this being that the effective dynamic magnetic field in Kramers salts is related to $\lambda\vec{L}\cdot\vec{S}$ and $\beta\vec{L}\cdot\vec{H}$, and not to $2\beta\vec{S}\cdot\vec{H}$. In other words, the relaxation results from the modulation of the anisotropic g factor. (b) The rotational modes of the crystalline complex may play an important role, even though the amplitude of vibration is weaker than that of the vibration modes. We will see indeed that the rotating motion of the orbitals can be essential in the relaxation process; this motion is generated by all the vibration modes (which also entail polarizations), but in particular by the purely rotational modes of the complex. (c) Another effect will result from the modulation of the orbital energy; this effect will be studied in an addendum [Phys. Rev. (to be published)].

I. INTRODUCTION

Since the work of Heitler and Teller[1] and Fierz[2] it has generally been admitted that spin-lattice relaxation in crystalline media is, principally, a process by which the modulated potential (generated by the thermal motion of the lattice atoms) supplies transitions between the spin eigenstates of the static Hamiltonian,[3] the energy difference being transferred to the lattice oscillators. This way of considering the problem implies the hypothesis by which the orbitals between which the transitions are induced do not follow adiabatically the displacements of the surrounding atoms. The aim of the present paper is to discuss this adiabaticity.

Our study is divided into six sections. In Sec. II, the principles on which spin-lattice relaxation in crystalline media is founded are briefly reviewed , and some aspects of these principles are criticized. In Sec. III, a new formulation of the problem is presented. Section IV gives a detailed comparison between the results obtained with the two theories. In Sec. V, the theory is applied to a simple model of crystalline lattice. It is shown that the vibrational modes act on the system by means of a modulation of orientation of the orbitals. In Sec. VI, a specific formulation to study spin-lattice relaxation through the rotating motion of the orbitals is presented and some applications of this formulation are given.

II. PRINCIPLES OF SPIN-LATTICE RELAXATION THEORY IN CRYSTALLINE MEDIA

A. Expression of Total Hamiltonian Operator

Let us consider a crystalline lattice in which paramagnetic ions are surrounded by diamagnetic ones producing at their level an electric potential V_c. The Hamiltonian describing the motion of the paramagnetic ion in interaction with the lattice and an applied magnetic field $\vec{H}$ can be written as follows:

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

where $\mathcal{H}_0$ represents the energy of the free ion, $2\beta\vec{S}\cdot\vec{H}$, $\beta\vec{L}\cdot\vec{H}$, and $\lambda\vec{L}\cdot\vec{S}$ are the spin Zeeman term, the orbital Zeeman term, and the spin-orbit coupling term, for this ion, V_c is the crystalline potential, and $\mathcal{H}_L$ is the lattice-vibration operator.

$\mathcal{H}_L$ can be expressed as a function of the creation and annihilation operators $a_{\vec{q}}$ and $a_{\vec{q}}^\dagger$ as follows[4,5]:

$$\mathcal{H}_L = \sum_{\vec{q}} \hbar\omega_{\vec{q}}(a_{\vec{q}}^\dagger a_{\vec{q}} + \tfrac{1}{2}), \tag{2}$$

where $\vec{q}$ is the wave vector of the acoustic waves, and $\omega_{\vec{q}}$ is the frequency of the qth mode.

The crystalline potential V_c depends on the thermal motion of the lattice ions and, thus, can be expanded in powers of the deformations, ϵ_{kl}, of the ionic complex. These deformations can, in turn, be written as functions of the creation and annihilation operators, as follows.

Let us denote by $\vec{R}_p^0$ the equilibrium position of an ion and by $\delta\vec{R}_p^0$ the displacement of this ion from equilibrium, we can write[5]

$$\delta\vec{R}_p^0 = \sum_{\vec{q}} e_{\vec{q}} (\hbar/2M\omega_{\vec{q}})^{1/2}\{a_{\vec{q}} e^{i\vec{q}\cdot\vec{R}_p^0} + a_{\vec{q}}^\dagger e^{-i\vec{q}\cdot\vec{R}_p^0}\} , \tag{3}$$

where M is the mass of the crystal.

The $\vec{e}_{\vec{q}}$ is the unit vector directed along the displacement associated with a mode.

The strain tensor around the site $\vec{R}_p^0$ will be written

$$\epsilon_{kl} = \tfrac{1}{2}\left(\frac{\partial\delta R_{pk}^0}{\partial R_{pl}^0} + \frac{\partial\delta R_{pl}^0}{\partial R_{pk}^0}\right) , \tag{4}$$

$$= \sum_{\vec{q}} (\hbar/2M\omega_{\vec{q}})^{1/2}\tfrac{1}{2} i(e_{\vec{q}k}\vec{q}_l + e_{\vec{q}l}\vec{q}_k)\{a_{\vec{q}} e^{i\vec{q}\cdot\vec{R}_p^0} - a_{\vec{q}}^\dagger e^{-i\vec{q}\cdot\vec{R}_p^0}\} , \tag{5}$$

where $k,\ l = x,\ y,\ z$.

Following Orbach[6,7] we can ignore the anisotropy and use an average strain.

The expansion of V_c in powers of the average strain can be written as

$$V_c = V_c^{(0)} + V_c^{(1)}\epsilon + V_c^{(2)}\epsilon^2 + \cdots , \tag{6}$$

where $V_c^{(0)}$ is the static interaction, which removes the orbital degeneracy. The terms depending on ϵ, play a role in the relaxation process discussed later.

B. Formulation of Nonadiabatic Theory

Many formulations of the nonadiabatic theory exist[7-10] which present some differences. We will not study the specific aspects of each of them, because we are specifically interested here in the role given to the dynamic crystalline potential and the magnetic operators of the system. As regards these operators, two alternative roles have been proposed, by Van Vleck[8] and Mattuck and Strandberg.[9] We first present a brief summary of the theory, following Mattuck and Strandberg, and then compare it with Van Vleck's formulation in so far as this is relevant to the problem.

In it's most general aspect, the nonadiabatic theory expresses the fact that the crystalline potential modulation, produced at the level of the paramagnetic ions, supplies transitions between the two lowest spin states of the static Hamiltonian. Two mechanisms are encountered: the direct process and the Raman process. The first one is generated by the linear term $V_c^{(1)}\epsilon$ introduced in formula (6). In such a case, spin relaxation is accompanied by the creation of a single phonon. This mechanism is thus predominant in the liquid-helium region.

Let us denote by Ψ_+ and Ψ_- the two lowest states of the Hamiltonian

$$\mathcal{H}_0 + 2\beta\vec{S}\cdot\vec{H} + \lambda\vec{L}\cdot\vec{S} + \beta\vec{L}\cdot\vec{H} + V_c^{(0)}$$

and N and $N+1$ two states of the lattice operator $\mathcal{H}_L$ which obey the energy conservation equation

$$E_+ - E_- = E_N - E_{N+1} . \tag{7}$$

The relaxation probability regarding the direct process will be

$$W_{-\to +} = (2\pi/\hbar)\left|\langle \Psi_- | V_c^{(1)} | \Psi_+ \rangle \langle N | \epsilon | N+1 \rangle\right|^2 \rho(E) \;, \tag{8}$$

where $\rho\,(E)$ is the density of the final states. The Raman process is generated by the quadratic term $V_c^{(2)}\,\epsilon^2$ and by the linear term taken twice using second-order perturbation theory; this mechanism is thus predominant at high temperatures. In this case, the spin relaxation is accompanied by the creation and annihilation of two phonons of different energies such that

$$E_+ - E_- = (E_N - E_{N+1}) - (E_{N'} - E_{N'+1}) \;. \tag{9}$$

The total transition probability resulting from this mechanism will be obtained by summing over all phonon modes.

Both processes being based upon the same assumption regarding the role of the crystalline potential, we will limit our study to the direct process, it being admitted that the considerations developed will be quite general and could be applied also to the Raman process.

The effects of the electronic Zeeman terms and the spin-orbit-coupling term are well known. The Zeeman terms play an essential role in the case of the Kramers salts in which the lowest states present a spin degeneracy which can be removed only by a magnetic field. The spin-orbit interaction will be essential in mixing the α and β functions, without which the relaxation would not be possible since the crystalline potential is a purely spatial operator.

The theory of Van Vleck differs from the one of Mattuck and Strandberg in two respects: First, the choice of the unperturbed operator is not the same. However, as pointed out by Mattuck and Strandberg,[9] what one chooses as the unperturbed system is a matter of convenience (such as simplicity, rapidity of convergence, and so on). So, this point does not change the results obtained with the two formulations. The second point which makes them different is the choice of initial and final states. We know, in fact, according to Karplus and Schwinger[9,11] that when a system is in an arbitrary state A at time $t=0$ and we wish to know the probability amplitude of some other state B, orthogonal to A at time t, we can write

$$P_{B\to A}(t) = \langle B | \exp[(it/\hbar)(\mathcal{H}_1 + \mathcal{H}_2)] | A \rangle \;, \tag{10}$$

where $\mathcal{H}_1 + \mathcal{H}_2$ is the total Hamiltonian operator, which does not depend on time.

There is an important difference here between the two formulations, since the second one takes the eigenfunctions of $\mathcal{H}_0 + 2\beta\vec{S}\cdot\vec{H} + V_c^{(0)} + \mathcal{H}_L$ as initial and final states, while the first one takes the eigenfunctions of

$$\mathcal{H}_0 + 2\beta\vec{S}\cdot\vec{H} + \beta\vec{L}\cdot\vec{H} + \lambda\vec{L}\cdot\vec{S} + V_c^{(0)} + \mathcal{H}_L \;. \tag{11}$$

Equation (10) shows clearly the importance of the choice of the eigenstates between which the transitions are induced. In fact, the two theories lead to equivalent results to the considered order of magnitude.

C. Criticism of Previous Formulations

As regards our problem, there is a point which is common to these two formulations: The functions between which the transitions are induced present an orbital part which is static with respect to the laboratory axes. The choice of such functions seems, however, questionable. It implies that when a spin transition takes place, the axis of quantization of orbitals does not follow the displacements of the crystalline complex. This hypothesis is in contradiction with the data of the problem. We know, in fact, that the motion of the lattice ions is very slow relative to the orbital motion of electrons; as a consequence, the orbitals of the unpaired electrons must adjust themselves adiabatically to the position of the crystalline complex.

On the other hand, the motion of the complex presents in its Fourier spectrum a component which corresponds to the resonance frequency of the spin. So that, the problem must be considered as follows: The modulated crystalline potential entails modulation of orientation and polarization of the orbitals. This orbital modulation generates a modulation of the effective magnetic field, which supplies the spin transitions. In consequence, the process involves two phenomena, which are superposed: One of them is adiabatic (the modulation of orbitals consecutive to the motion of ionic complex) and the other is not (the spin transition).

The whole problem consists therefore of the calculation of the spin Hamiltonian with the modulated wave functions, and then the separation of it into a sum of two terms, one of them being static and the other modulated. Only the second will be useful in the calculation of the relaxation probability.

Two formalisms can be used to perform this calculation: the semiclassical formalism and the quantum-mechanical one. In previous papers[12,13] the first one had been proposed. We now present a quantum-mechanical description of the problem.

III. FORMULATION OF ADIABATIC QUANTUM THEORY

Consider the Hamiltonian given by formula (1). We have to determine the dynamic spin Hamiltonian of the system. We limit our description to the direct process for the reason previously given. The most simple and general way to determine the effective Hamiltonian $\mathcal{H}_{\mathrm{eff}}$ of the system is to use the classical formula[14,15]

$$\langle 0'|\mathcal{H}_{\mathrm{eff}}|0\rangle=\sum_n\frac{\langle 0'|\mathcal{H}_{\mathrm{pert}}|n\rangle\langle n|\mathcal{H}_{\mathrm{pert}}|0\rangle}{\Delta_{0n}}+\langle 0'|2\beta S_z H_z|0\rangle, \tag{12}$$

where $\mathcal{H}_{\mathrm{pert}}=\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}+\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}$, $|0\rangle$ and $|0'\rangle$ are the ground and first excited states of the Hamiltonian not perturbed by the magnetic operators, $|n\rangle$ is any other excited state, and $\Delta_{0n}=E_0-E_n$.

In most cases, a perturbation treatment will be used. Let us compute the eigenfunctions of the Hamiltonian $\mathcal{H}_0+V_c^{(0)}+V_c^{(1)}\epsilon$, using the stationary-perturbation theory for a nondegenerate level. We obtain

$$\begin{aligned}|0\rangle&=\varphi_0\alpha+\Sigma_i\,(\langle\varphi_i|V_c^{(1)}\epsilon|\varphi_0\rangle/\Delta_{0i})\varphi_i\alpha+\cdots,\\ |n\rangle&=\varphi_n\sigma+\Sigma_i\,(\langle\varphi_i|V_c^{(1)}\epsilon|\varphi_n\rangle/\Delta_{ni})\varphi_i\sigma+\cdots,\\ |0'\rangle&=\varphi_0\beta+\Sigma_i\,(\langle\varphi_i|V_c^{(1)}\epsilon|\varphi_0\rangle/\Delta_{0i})\varphi_i\beta+\cdots,\end{aligned} \tag{13}$$

where the $\varphi_i\sigma$'s are the eigenstates of $\mathcal{H}_0+V_c^{(0)}$. α and β can be the two spin states of a Kramers doublet, but they can also designate any two spin states of a paramagnetic system with multiplicity different from 2.

Starting from these functions, let us compute the dynamic part of the effective Hamiltonian. To do so, we will replace $|0\rangle|0'\rangle$ and $|n\rangle$ in (12) by their values from (13) and keep only those terms containing the dynamic crystalline potential. If we take into account only the terms inversely proportional to the square of the energy, we obtain[16]

$$\begin{aligned}\tilde{\sum}_n(\langle 0'|\mathcal{H}_{\mathrm{pert}}|n\rangle\langle n|\mathcal{H}_{\mathrm{pert}}|0\rangle/\Delta_{0n})&=\sum_{n\sigma}\Big[\langle\varphi_0\beta|\mathcal{H}_{\mathrm{pert}}|\varphi_n\sigma\rangle\\ &\times\Big\langle\sum_j(\langle\varphi_j|V_c^{(1)}\epsilon|\varphi_n\rangle/\Delta_{nj}\Delta_{0n})\varphi_j\sigma\Big|\mathcal{H}_{\mathrm{pert}}\Big|\varphi_0\alpha\Big\rangle\\ &+\langle\varphi_0\beta|\mathcal{H}_{\mathrm{pert}}|\varphi_n\sigma\rangle\\ &\times\Big\langle\varphi_n\sigma\Big|\mathcal{H}_{\mathrm{pert}}\Big|\sum_j(\langle\varphi_j|V_c^{(1)}\epsilon|\varphi_0\rangle/\Delta_{0j}\Delta_{0n})\varphi_j\alpha\Big\rangle\\ &+\Big\langle\sum_j(\langle\varphi_j|V_c^{(1)}\epsilon|\varphi_0\rangle/\Delta_{0j}\Delta_{0n})\varphi_j\beta\Big|\mathcal{H}_{\mathrm{pert}}\Big|\varphi_n\sigma\Big\rangle\\ &\times\langle\varphi_n\sigma|\mathcal{H}_{\mathrm{pert}}|\varphi_0\alpha\rangle\\ &+\Big\langle\varphi_0\beta\Big|\mathcal{H}_{\mathrm{pert}}\Big|\sum_j(\langle\varphi_j|V_c^{(1)}\epsilon|\varphi_n\rangle/\Delta_{nj}\Delta_{0n})\varphi_j\sigma\Big\rangle\\ &\times\langle\varphi_n\sigma|\mathcal{H}_{\mathrm{pert}}|\varphi_0\alpha\rangle\Big],\end{aligned} \tag{14}$$

where $\tilde{\sum}$ means that only terms containing the modulated potential have been kept in the summation, and σ is a spin function. We can expand this expression into

$$\begin{aligned}&\sum_{jn\sigma}\{(1/\Delta_{0n}\Delta_{nj})[V_c^{(1)}\epsilon_{nj}(\langle\varphi_0\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_n\sigma\rangle\langle\varphi_j\sigma|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_0\alpha\rangle+\langle\varphi_0\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_n\sigma\rangle\langle\varphi_j|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_0\rangle\\ &\quad+\langle\varphi_0|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_n\rangle\langle\varphi_j\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_0\alpha\rangle)\\ &\quad+V_c^{(1)}\epsilon_{jn}(\langle\varphi_0\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_j\sigma\rangle\langle\varphi_n\sigma|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_0\alpha\rangle+\langle\varphi_0\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_j\alpha\rangle\\ &\quad\times\langle\varphi_n|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_0\rangle+\langle\varphi_0|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_j\rangle\langle\varphi_n\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_0\alpha\rangle)]+(1/\Delta_{0n}\Delta_{0j})[V_c^{(1)}\epsilon_{j0}(\langle\varphi_0\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_n\sigma\rangle\\ &\quad\times\langle\varphi_n\sigma|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_j\alpha\rangle+\langle\varphi_0\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_n\sigma\rangle\langle\varphi_n|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_j\rangle+\langle\varphi_0|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_n\rangle\langle\varphi_n\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_j\alpha\rangle)\\ &\quad+V_c^{(1)}\epsilon_{0j}(\langle\varphi_j\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_n\sigma\rangle\langle\varphi_n\sigma|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_0\alpha\rangle+\langle\varphi_j\beta|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\varphi_n\alpha\rangle\langle\varphi_n|\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}|\varphi_0\rangle\\ &\quad+\langle\varphi_j|\beta\mathrm{L}\cdot\mathrm{H}|\varphi_n\rangle\langle\varphi_n\beta|\lambda\mathrm{L}\cdot\mathrm{S}|\varphi_0\alpha\rangle)]\}.\end{aligned} \tag{15}$$

This expression reduces to $\langle\beta|\tilde{\mathcal{H}}_S|\alpha\rangle$ and then the transition matrix element will be

$$\langle N|\epsilon|N+1\rangle\langle\beta|\tilde{\mathcal{H}}_S|\alpha\rangle, \tag{16}$$

where $\tilde{\mathcal{H}}_S$ is the dynamic part of the spin Hamiltonian and βN and $\alpha(N+1)$ are two states of the static Hamiltonian $\mathcal{H}_S+\mathcal{H}_L$. In the special case of the Kramers doublets, it can be written

$$\langle N|\epsilon|N+1\rangle\langle\beta|\beta\vec{\mathrm{S}}\cdot\tilde{\mathcal{G}}\cdot\vec{\mathrm{H}}|\alpha\rangle \tag{17a}$$

where $\frac{1}{2}\tilde{\mathcal{G}}\cdot\mathrm{H}$ is the dynamic effective field for the system.

The relaxation probability will be calculated by means of the time-dependent perturbation theory.[17] Its expression will reduce to

$$W_{\beta N\to\alpha(N+1)}=(2\pi/\hbar)\,|\langle\beta|\tilde{\mathcal{H}}_s|\alpha\rangle|^2\times|\langle N|\epsilon|N+1\rangle|^2\rho(E), \tag{17b}$$

where $\rho(E)$ is the density of final states.

IV. COMPARISON BETWEEN RESULTS OBTAINED WITH ADIABATIC AND NONADIABATIC THEORIES

Let us compute the transition matrix element obtained by means of the nonadiabatic theory and compare the results obtained, respectively, with the two methods.

Applying the theory of perturbations to second order, we obtain for the transition matrix element

$$\begin{aligned}
&\langle\varphi_0\beta+\sum_{j,\sigma}\frac{\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_0\beta\rangle}{\Delta_{0\beta,j\sigma}}\varphi_{j\sigma}+\sum_{n}\frac{\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle}{\Delta_{0n}}\varphi_n\beta\\
&+\sum_{\substack{jn\\ \sigma\sigma'}}\frac{\langle\varphi_n\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_j\sigma'\rangle\langle\varphi_j\sigma'|\lambda\vec{L}\cdot\vec{S}|\varphi_0\beta\rangle}{\Delta_{0\beta,j\sigma'}\Delta_{0\beta,n\sigma}}\varphi_n\sigma+\sum_{jn\sigma}\frac{\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_j\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_0\beta\rangle}{\Delta_{0\beta,n\sigma}\Delta_{0\beta,j\sigma}}\varphi_n\sigma\\
&+\sum_{jn\sigma}\frac{\langle\varphi_n\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_j\beta\rangle\langle\varphi_j|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle}{\Delta_{n\sigma,j\beta}\Delta_{0\beta,n\sigma}}\varphi_n\sigma+\sum_{jn\sigma}\frac{\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_n\beta\rangle}{\Delta_{0\beta,n\alpha}\Delta_{n\beta,j\sigma}}\varphi_j\sigma+\cdots|V_c^{(1)}|\varphi_0\alpha\\
&+\sum_{k,\sigma'}\frac{\langle\varphi_k\sigma'|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle}{\Delta_{0\alpha,k\sigma'}}\varphi_k\sigma'+\sum_{l}\frac{\langle\varphi_l|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle}{\Delta_{0l}}\varphi_l\beta+\sum_{\substack{jn\\ \sigma\sigma'}}\frac{\langle\varphi_n\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_j\sigma'\rangle\langle\varphi_j\sigma'|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle}{\Delta_{0\alpha,j\sigma'}\Delta_{0\alpha,n\sigma}}\varphi_n\sigma\\
&+\sum_{jn\sigma}\frac{\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_j\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle}{\Delta_{0\alpha,n\sigma}\Delta_{0\alpha,j\sigma}}\varphi_n\sigma+\sum_{jn\sigma}\frac{\langle\varphi_n\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_j\alpha\rangle\langle\varphi_j|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle}{\Delta_{n\sigma,j\alpha}\Delta_{0\alpha,n\sigma}}\varphi_n\sigma\\
&+\sum_{jn\sigma}\frac{\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_n\alpha\rangle}{\Delta_{0\alpha,n\alpha}\Delta_{n\alpha,j\sigma}}\varphi_j\sigma+\cdots\rangle\langle N|\epsilon|N+1\rangle\quad. \qquad (18)
\end{aligned}$$

In order to compare the roles played by $\lambda\vec{L}\cdot\vec{S}$ and $\beta\vec{L}\cdot\vec{H}$ in the two theories we neglect the terms $\Delta_{\alpha\beta}$ in the expansion of the denominators.

The expression (18) then may be reduced to

$$\begin{aligned}
&\sum_{jn\sigma}\{(1/\Delta_{0n}\Delta_{0j})[V_c^{(1)}{}_{nj}(\langle\varphi_0\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_n\sigma\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle+\langle\varphi_0\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_n\alpha\rangle\langle\varphi_j|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle\\
&+\langle\varphi_0|\beta\vec{L}\cdot\vec{H}|\varphi_n\rangle\langle\varphi_j\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle)+V_c^{(1)}{}_{0n}(\langle\varphi_n\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_j\sigma\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle\\
&+\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_j\rangle\langle\varphi_j\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_0\alpha\rangle)+V_c^{(1)}{}_{n0}(\langle\varphi_0\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_j\sigma\rangle\langle\varphi_j\sigma|\lambda\vec{L}\cdot\vec{S}|\varphi_n\alpha\rangle\\
&+\langle\varphi_0\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_j\alpha\rangle\langle\varphi_j|\beta\vec{L}\cdot\vec{H}|\varphi_n\rangle)]+(1/\Delta_{0n}\Delta_{nj})[\langle\varphi_n\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_j\alpha\rangle\langle\varphi_j|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle V_c^{(1)}{}_{0n}\\
&+\langle\varphi_0|\beta\vec{L}\cdot\vec{H}|\varphi_j\rangle\langle\varphi_j\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_n\alpha\rangle V_c^{(1)}{}_{n0}+\langle\varphi_n|\beta\vec{L}\cdot\vec{H}|\varphi_0\rangle\langle\varphi_j\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_n\alpha\rangle V_c^{(1)}{}_{0j}\\
&+\langle\varphi_n\beta|\lambda\vec{L}\cdot\vec{S}|\varphi_j\alpha\rangle\langle\varphi_0|\beta\vec{L}\cdot\vec{H}|\varphi_n\rangle V_c^{(1)}{}_{j0}]\}\langle N|\epsilon|N+1\rangle\;\cdot \qquad (19)
\end{aligned}$$

Replacing Δ_{nj} by $(\Delta_{n0}-\Delta_{j0})$, we can see that the expressions (15) and (19) are equal. This equality results from the fact that we have neglected the contribution of the spin Zeeman term at the denominators of expression (18). In fact this contribution is of the same order as that due to the orbital Zeeman term, in Van Vleck's theory. On the contrary, this term does not play a role in the adiabatic theory, as can be seen from formula (12).

This can be interpreted when we consider that spin-lattice relaxation in Kramers salts results from the modulation of the anisotropic g factor which is related to $\lambda\vec{L}\cdot\vec{S}$ and $\beta\vec{L}\cdot\vec{H}$ (and not to $2\beta\vec{S}\cdot\vec{H}$), and is in agreement with various experimental studies in this field and theoretical studies in other systems.[18–20] According to these, T_1 varies as $1/(\Delta g)^2$. (A similar expression is obtained by means of the adiabatic theory, as will be shown at the end of Sec. VI.) We know that the rotations play an important role in this g-factor modulation, and an example will be given in which they might be predominant. We will also see that the nonrotational modes of the crystalline complex can generate a relaxation process through the rotating motion of the orbitals.

V. APPLICATION OF THEORY TO SIMPLE MODEL OF CRYSTALLINE LATTICE

Consider a model of cystalline lattice in which paramagnetic ions with spin $S=\frac{1}{2}$ are included and assume that the fundamental eigenfunctions of $\mathcal{H}_0$ are p orbitals. The energy associated with these orbitals presents a degeneracy of third order, which is removed by the static potential $V_c^{(0)}$. Let

θ_m and φ_m be the directional angles of the applied magnetic field $\vec{\mathrm{H}}$ in the (x', y', z') crystal frame.[21]

The eigenfunctions of $\mathcal{H}_0 + 2\beta\vec{\mathrm{S}}\cdot\vec{\mathrm{H}} + V_c^{(0)}$ will be

$$
\begin{aligned}
p_{z'}\sigma &= (p_z\cos\theta_m - p_x\sin\theta_m)\sigma\ ,\\
p_{y'}\sigma &= (p_x\cos\theta_m\sin\varphi_m\\
&\qquad + p_y\cos\varphi_m + p_z\sin\theta_m\sin\varphi_m)\sigma\ , \qquad (20)\\
p_{x'}\sigma &= (p_x\cos\theta_m\cos\varphi_m\\
&\qquad - p_y\sin\varphi_m + p_z\sin\theta_m\cos\varphi_m)\sigma\ ,
\end{aligned}
$$

where σ is a function of spin (α or β). We suppose that $p_{z'}$ is the lowest orbital of the system and $p_{x'}$ and $p_{y'}$ degenerate. As a consequence, the g tensor will be axial.

We use stationary-perturbation theory to compute the first-order contributions of $V_c^{(1)}\epsilon$. The two functions of lowest orbital energy will be

$$
\begin{aligned}
\Phi\alpha = {} & (p_z\cos\theta_m - p_x\sin\theta_m)\,\alpha\\
& -\{[(V_c^{(1)}\epsilon_{xz}/\Delta)\cos(2\theta_m)\cos\theta_m]p_x\\
& + [(V_c^{(1)}\epsilon_{yz}/\Delta)\cos\theta_m - (V_c^{(1)}\epsilon_{xy}/\Delta)\sin\theta_m]p_y\\
& + [(V_c^{(1)}\epsilon_{xz}/\Delta)\cos(2\theta_m)\sin\theta_m]p_z\}\,\alpha\ , \qquad (21)
\end{aligned}
$$

$$
\begin{aligned}
\Phi\beta = {} & (p_z\cos\theta_m - p_x\sin\theta_m)\,\beta\\
& -\{[(V_c^{(1)}\epsilon_{xz}/\Delta)\cos2\theta_m\cos\theta_m]p_x\\
& + [(V_c^{(1)}\epsilon_{yz}/\Delta)\cos\theta_m - (V_c^{(1)}\epsilon_{xy}/\Delta)\sin\theta_m]p_y\\
& + [(V_c^{(1)}\epsilon_{xz}/\Delta)\cos2\theta_m\sin\theta_m]p_z\}\,\beta\ , \qquad (22)
\end{aligned}
$$

where Δ is the energy difference between the excited and the ground states.

Starting from these functions, we may compute the dynamic spin Hamiltonian for the system. Here, the system is a Kramers doublet, so that this Hamiltonian may be determined by a method slightly different from that developed in Sec. III, Ref. 14. It consists in computing the off-diagonal matrix elements of $\lambda\,\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}$ with the functions $\Phi\alpha$ and $\Phi\beta$ first perturbed by $\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}$ which will be called $\Psi\alpha$ and $\Psi\beta$.

Keeping only those terms linear in $V_c^{(1)}\epsilon$ and $\beta\,\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}$ (Ref. 22) we obtain

$$
\begin{aligned}
&\langle(p_z\cos\theta_m - p_x\sin\theta_m)\,\alpha\,|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\,(\beta H_z/\Delta^2)\\
&\quad\times V_c^{(1)}\epsilon_{xz}(i\cos2\theta_m\cos\theta_m)\,\beta p_y\rangle\\
&\quad+\langle(\beta H_z/\Delta^2)\,V_c^{(1)}\epsilon_{xz}(i\cos2\theta_m\cos\theta_m)\\
&\quad\times\alpha p_y|\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|(p_z\cos\theta_m - p_x\sin\theta_m)\beta\rangle\\
&\quad+\langle V_c^{(1)}\epsilon_{xz}(\cos2\theta_m\sin\theta_m)\\
&\quad\times p_z\alpha\,|\lambda\,\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\,(\beta H_z/\Delta^2)(-i\sin\theta_m)\,p_y\beta\rangle\\
&\quad+\langle(\beta H_z/\Delta^2)\,(-i\sin\theta_m)\,p_y\alpha\,|\lambda\,\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}|\\
&\quad\times V_c^{(1)}\epsilon_{xz}(\cos2\theta_m\sin\theta_m)\,p_z\beta\rangle\ . \qquad (23)
\end{aligned}
$$

The calculation of the transition matrix element gives

$$-(\lambda\beta H_z/\Delta^2)\,V_c^{(1)}{}_{xz}\cos^2 2\theta_m\langle N+1|\epsilon|N\rangle\,. \qquad (24)$$

With the help of this formula, we may compute the relaxation probability regarding the direct process, and we obtain

$$
\begin{aligned}
W_{(N+1)\alpha\to N\beta} = {} & \frac{2\pi}{\hbar}\,\frac{\lambda^2\beta^2H^2}{\Delta^4}(V_c^{(1)}{}_{xz})^2\cos^4 2\theta_m\\
& \times|\langle N+1|\epsilon|N\rangle|^2\rho(E)\ . \qquad (25)
\end{aligned}
$$

Here an important remark can be made. If we neglect the terms proportional to py in Eq. (22), which do not play a role in the computation of the relaxation probability [cf. Eq. (23)], then the perturbed orbitals $\Phi\alpha$ and $\Phi\beta$ can be deduced from the static ones by a rotation of an angle equal to

$$(V_c^{(1)}\epsilon_{xz}/\Delta)\,\cos2\theta_m\ . \qquad (26)$$

To show this, we must take into account the fact that a change in orientation of $p_{z'}$ by an angle $\tilde{\theta}$ changes this orbital into

$$p_z\,\cos(\theta_m+\tilde{\theta}) - p_x\,\sin(\theta_m+\tilde{\theta})\ ,$$

which can be expanded to first order[23] as follows:

$$p_z(\cos\theta_m - \sin\theta_m\,\tilde{\theta}) - p_x(\sin\theta_m + \cos\theta_m\,\tilde{\theta}). \qquad (27)$$

After identification of the orbital part of (22) and (27), we obtain the expression (26). We can see that if we limit our perturbation expansion of the eigenfunctions of $\mathcal{H}_0 + V_c$ to the subspace of functions of $\mathcal{H}_0 + V_c^{(0)}$ possessing the same L^2,[24] the g-tensor modulation will essentially result from a modulation of orientation of the orbitals. It is likely that the rotational modes of the complex will play an important role in this modulation. This might be true even though the modulated crystalline potential generated by the rotational modes was weaker than that of other modes.

We now develop a method to study spin-lattice relaxation through rotating motion of the orbitals.[25]

VI. QUANTUM-MECHANICAL FORMULATION OF SPIN-LATTICE RELAXATION THROUGH ROTATING MOTION OF ORBITALS

A. General Aspects

In order to deal with the problem, we use a formalism which is of practical interest, because it can be applied to all crystals in the same way. It avoids the explicit computation of the modulated potential and modulated orbitals, and consists in using two quantization axes to express the magnetic operators. This method will be presented in its general form.

Let us consider a crystalline complex centered on a paramagnetic ion, and study the rotating motion of this complex around the ion. We call x', y', z' a frame connected to the complex and x, y, z a frame whose z axis is along the magnetic field $\vec{H}$ and whose x axis is at the intersection of the plane perpendicular to z and the (x', y') plane [this amounts to taking $\psi(t)=0$ at every instant, since the angle ψ has no effect on the phenomenon].

If the complex were static, the wave functions would be quantized by a frame connected to the entire crystal. On the other side – the complex describing, say, a purely rotating motion – two cases may be considered: (a) If the velocity of the ions were of the same order as the orbital motion of the electrons, the wave functions would not instantaneously follow the complex (this would be the nonadiabatic cases). (b) When the motion of the ions is very slow relative to that of the electrons, the wave functions adjust themselves almost instantaneously to the orientation of the complex. Only this second case will interest us. The problem must then be treated as if the orbitals of the central ion were quantized by the axes of the complex, while the spin is still quantized by the external magnetic field.

Let us express the spin operators in the frame of the laboratory and the space operators in the frame of the crystalline complex. The spin-orbit interaction will then be written:

$$\begin{aligned}\mathcal{H}_{LS}=\lambda\{&L_{x'}(S_x\cos\theta\sin\varphi-S_y\sin\varphi\\&+S_z\sin\theta\cos\varphi)+L_{y'}(S_x\cos\theta\sin\varphi+S_y\cos\varphi\\&+S_z\sin\theta\sin\varphi)+L_{z'}(-S_x\sin\theta+S_z\cos\theta)\}\,,\end{aligned}\tag{28}$$

and the orbital Zeeman interaction will be[26]

$$\begin{aligned}\mathcal{H}_{OZ}=\beta H_z(&L_{x'}\sin\theta\cos\varphi\\&+L_{y'}\sin\theta\sin\varphi+L_{z'}\cos\theta)\;.\end{aligned}\tag{29}$$

Since the orientation of the complex is modulated, θ and φ can be considered as a sum of two terms:

$$\begin{aligned}&\theta=\theta_m+\tilde{\theta}\,,\\&\varphi=\varphi_m+\tilde{\varphi},\end{aligned}\tag{30}$$

where (θ_m, φ_m) defines the average orientation of the complex relative to the laboratory axes and $(\tilde{\theta}, \tilde{\varphi})$ is the deviation of this orientation from its average value. Using a Taylor expansion of $\sin\theta$, $\sin\varphi$, $\cos\theta$, $\cos\varphi$ restricted to the first two terms, we get, for the magnetic operators[27]

$$\mathcal{H}_{LS}+\mathcal{H}_{OZ}=M+\tilde{M}\,,$$

where

$$\begin{aligned}M=\beta\,(&L_{x'}H_z\sin\theta_m\cos\varphi_m\\&+L_{y'}H_z\sin\theta_m\sin\varphi_m)\\&+\lambda\,(L_{x'}S_x\cos\theta_m\cos\varphi_m\\&-L_{x'}S_y\sin\varphi_m\\&+L_{x'}S_z\sin\theta_m\cos\varphi_m\\&+L_{y'}S_x\cos\theta_m\sin\varphi_m\\&+L_{y'}S_y\cos\varphi_m+L_{y'}S_z\sin\theta_m\sin\varphi_m)\,,\end{aligned}\tag{31}$$

$$\begin{aligned}\tilde{M}=\beta(&-L_{x'}H_z\sin\theta_m\sin\varphi_m\tilde{\varphi}\\&+L_{x'}H_z\cos\theta_m\cos\varphi_m\tilde{\theta}\\&+L_{y'}H_z\sin\theta_m\cos\varphi_m\tilde{\varphi}\\&+L_{y'}H_z\cos\theta_m\sin\varphi_m\tilde{\theta})\\&-\lambda(L_{x'}S_x\sin\theta_m\cos\varphi_m\tilde{\theta}\\&+L_{x'}S_x\cos\theta_m\sin\varphi_m\tilde{\varphi}\\&+L_{x'}S_y\cos\varphi_m\tilde{\varphi}-L_{y'}S_x\cos\theta_m\cos\varphi_m\tilde{\varphi}\\&+L_{y'}S_x\sin\theta_m\sin\varphi_m\tilde{\theta}\\&+L_{y'}S_y\sin\varphi_m\tilde{\varphi})\;.\end{aligned}\tag{32}$$

These expressions are quite general and can be used wherever the relaxation through modulation of orientation is encountered. The Hamiltonian can thus be written

$$\mathcal{H}=\mathcal{H}_0+2\beta S_zH_z+M+\tilde{M}+V_c^{(0)}+V_c'^{(1)}\epsilon\;,\tag{33}$$

where $V_c'^{(1)}\epsilon$ has not the same meaning as $V_c^{(1)}\epsilon$, since it does not include the modulation of the crystalline potential through the rotational modes.

In fact, the nonrotational modes will also entail a relaxation process through rotating motion of the orbitals. In some cases, as in the example given in Sec. V, this process will be predominant, and it will be possible to include $V_c^{(1)}\epsilon$ in the modulated angles.

The angles $\tilde{\theta}$ and $\tilde{\varphi}$ will then be replaced by $\tilde{\theta}'$ and $\tilde{\varphi}'$, and $V_c'^{(1)}\epsilon$ will be removed altogether from the Hamiltonian.

The modulated angles will be expressed as functions of the creation and annihilation operators, and the total transition probability for the direct process will be[28]

$$\begin{aligned}P_{+N\to-N+1}=&(2\pi/\hbar)\\&\times\left|\langle\Psi_+N|\tilde{M}|\Psi_-(N+1)\rangle\right|\rho(E)\;,\end{aligned}\tag{34}$$

where N and $N+1$ are two eigenstates of the lattice operator obeying the energy conservation equation, and Ψ_+ and Ψ_- are the eigenfunctions of $\mathcal{H}_0+V_c^{(0)}+2\beta S_zH_z+M$.

B. Application to Simple Model of Crystalline Lattice

Let us apply the method of separate quantization just defined to the system considered in Sec. V. We obtain for Ψ_+ and Ψ_-

$$\Psi_+ = p_{z'}\,\alpha + \sum_{i\sigma} \frac{\langle p_{i'}\sigma | M | p_{z'}\,\alpha\rangle p_{i'}\sigma}{E_{z'\alpha} - E_{i'\sigma}}, \tag{35}$$

$$\Psi_- = p_{z'}\beta + \sum_{i\sigma} \frac{\langle p_{i'}\sigma | M | p_{z'}\beta\rangle p_{i'}\sigma}{E_{z'\beta} - E_{i'\sigma}}. \tag{36}$$

Starting from these functions, and neglecting in the denominators the energy difference between the spin states whose contribution is negligible,[29] we get, for the matrix element of $\tilde{M}$,

$$\begin{aligned}\langle\Psi_+|\tilde{M}|\Psi_-\rangle &= 2\beta H_z\lambda \sin\theta_m \sin\varphi_m \cos\theta_m \cos\varphi_m(\tilde{\varphi}/\Delta E_{x'z'}) - i\beta H_z\lambda \sin\theta_m \cos^2\varphi_m(\tilde{\varphi}/\Delta E_{x'z'})\\ &+ \beta H_z\lambda\cos^2\theta_m\sin^2\varphi_m(\tilde{\theta}/\Delta E_{x'z'}) - i\beta H_z\lambda\cos\varphi_m\cos\theta_m\sin\varphi_m(\tilde{\theta}/\Delta E_{x'z'}) - \beta H_z\lambda\sin^2\theta_m\sin^2\varphi_m(\tilde{\theta}/\Delta E_{x'z'})\\ &+ i\beta H_z\lambda\sin\theta_m\sin^2\varphi_m(\tilde{\varphi}/\Delta E_{x'z'}) - 2\beta H_z\lambda\sin\theta_m\cos\theta_m\sin\varphi_m\cos\varphi_m(\tilde{\varphi}/\Delta E_{y'z'})\\ &- i\beta H_z\lambda\sin\theta_m\sin^2\varphi_m(\tilde{\varphi}/\Delta E_{y'z'}) + \beta H_z\lambda\cos^2\theta_m\cos^2\varphi_m(\tilde{\theta}/\Delta E_{y'z'}) + i\beta H_z\lambda\cos\varphi_m\cos\theta_m\sin\varphi_m(\tilde{\theta}/\Delta E_{y'z'})\\ &- \beta H_z\lambda\sin^2\theta_m\cos^2\varphi_m(\tilde{\theta}/\Delta E_{y'z'}) + i\beta H_z\lambda\sin\theta_m\cos^2\varphi_m(\tilde{\theta}/\Delta E_{y'z'}),\end{aligned} \tag{37}$$

where $\Delta E_{i'z'}$ is the energy difference between the i' and the ground levels. This expression depends on both θ and φ because the system is not axial.

If we suppose that $\Delta E_{x'z'} = \Delta E_{y'z'}$, this expression reduces to

$$\langle\Psi_+|\tilde{M}|\Psi_-\rangle = (\lambda\beta H_z\tilde{\theta}/\Delta)\cos 2\theta_m . \tag{38}$$

The relaxation probability will thus take the following form[30]:

$$W = (2\pi/\hbar)(\Delta g)^2\beta^2 H_z^2 \cos^2 2\theta_m |\langle N|\tilde{\theta}|N+1\rangle|^2 \rho(E) . \tag{39}$$

The method of separate quantization just described, is useful for experimental investigations. It gives the orientation dependance of the relaxation probability without knowing the explicit form for the modulated potential.

C. Study of Ti³⁺ Ion

We now apply the method of separate quantization to the case of the Ti^{3+} ion[31] included in an octahedral complex offering a trigonal distortion (an example of such a complex is titanium triacetylacetonate). The eigenfunctions describing the unpaired electron (not perturbed by the applied magnetic field, the spin-orbit operator, and the crystalline modulated potential) can be written as follows (see Fig. 1):

$$\begin{aligned}|t_0\rangle &= |0\rangle ,\\ |t_+\rangle &= (\tfrac{1}{3})^{1/2}|1\rangle + (\tfrac{2}{3})^{1/2}|-2\rangle ,\\ |t_-\rangle &= (\tfrac{1}{3})^{1/2}|-1\rangle - (\tfrac{2}{3})^{1/2}|2\rangle ,\\ |e_+\rangle &= (\tfrac{2}{3})^{1/2}|1\rangle - (\tfrac{1}{3})^{1/2}|-2\rangle ,\\ |e_-\rangle &= (\tfrac{2}{3})^{1/2}|-1\rangle + (\tfrac{1}{3})^{1/2}|2\rangle ,\end{aligned} \tag{40}$$

where

$$\begin{aligned}|2\rangle &= |-2\rangle^* = (15/8\pi)^{1/2} f(r) \times \tfrac{1}{4}\sin^2\theta e^{2i\varphi} ,\\ |1\rangle &= -|-1\rangle^* = (15/8\pi)^{1/2} f(r) \times (-\sin\theta\cos\varphi e^{i\varphi}),\\ |0\rangle &= (15/8\pi)^{1/2} f(r) 6^{-1/2}(3\cos^2\theta - 1).\end{aligned} \tag{41}$$

Taking the magnetic static operator M as a perturbation, we obtain the eigenfunctions of $\mathcal{H}_0 + V_c^{(0)} + M$.

These functions can be written

$$\begin{aligned}\Psi_{(+)} = |t_0\rangle &+ (k - il + m - in)\{|t_+\alpha\rangle/\delta + \sqrt{2}(|e_+\alpha\rangle/\Delta)\}\\ &+ (c - id + e - if)\{|t_+\beta\rangle/\delta + \sqrt{2}(|e_+\beta\rangle/\Delta)\}\\ &+ (k + il + m + in)\{|t_-\alpha\rangle/\delta + \sqrt{2}(|e_-\alpha\rangle/\Delta)\}\\ &+ (c - id - e + if)\{|t_-\beta\rangle/\delta + \sqrt{2}(|e_-\beta\rangle/\Delta)\} ,\end{aligned} \tag{42}$$

$$\begin{aligned}\Psi_{(-)} = |t_0\rangle &+ (k - il - m + in)\{|t_+\beta\rangle/\delta + \sqrt{2}(|e_+\beta\rangle/\Delta)\}\\ &+ (c + id - e - if)\{|t_+\alpha\rangle/\delta + \sqrt{2}(|e_+\alpha\rangle/\Delta)\}\\ &+ (k + il - m - in)\{|t_-\beta\rangle/\delta + \sqrt{2}(|e_-\beta\rangle/\Delta)\}\\ &+ (c + id + e + if)\{|t_-\alpha\rangle/\delta + \sqrt{2}(|e_-\alpha\rangle/\Delta)\} ,\end{aligned}$$

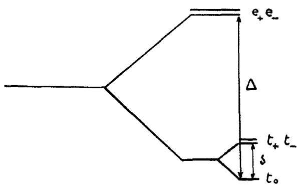

FIG. 1. Crystal-field splittings in an octahedral complex with a trigonal distortion.

where
$$\begin{aligned} k &= \tfrac{1}{2}\beta H_z \sin\theta_m \cos\varphi_m\,, \\ l &= \tfrac{1}{2}\beta H_z \sin\theta_m \sin\varphi_m\,, \\ m &= (\lambda/2\sqrt{2}) \sin\theta_m \cos\varphi_m\,, \\ n &= (\lambda/2\sqrt{2}) \sin\theta_m \sin\varphi_m\,, \\ c &= (\lambda/2\sqrt{2}) \cos\theta_m \cos\varphi_m, \quad d = (\lambda/2\sqrt{2}) \sin\varphi_m, \\ e &= (\lambda/2\sqrt{2}) \cos\varphi_m, \quad f = (\lambda/2\sqrt{2}) \cos\theta_m \sin\varphi_m\,. \end{aligned} \tag{43}$$

The transition matrix element of $\tilde{M}$ will be

$$\langle \Psi_{(+)} | \tilde{M} | \Psi_{(-)} \rangle = \{ 1/\delta + 2/\Delta \} (\lambda \beta H_z \cos 2\theta_m) \tilde{\theta}\,. \tag{44}$$

We can see that the angular dependance is exactly the same as in the model previously studied. This is related to the fact that the g tensors of both systems are axial, and that the ground state of $\mathcal{H}_0 + V_c^{(0)}$ in this model is a d_z^2 orbital.

This element can also be expressed as a function of the anisotropy of the g tensor[32] $\Delta g = \lambda(2/\delta + 4/\Delta)$:

$$\langle \Psi_{(+)} | \tilde{M} | \Psi_{(-)} \rangle = (\Delta g \beta H_z \cos 2\theta_m) \tilde{\theta}\,. \tag{45}$$

The transition probability will be

$$W = (2\pi/\hbar)(\Delta g)^2 \beta^2 H_z^2 \cos^2 2\theta_m |\langle N+1 | \tilde{\theta} | N \rangle|^2 \rho(E)\,. \tag{46}$$

This equation is identical to Eq. (43); this suggests that for complexes possessing the same amplitude of modulation and the same density of final states, the relaxation probability will be proportional to Δg^2 in conformity with the work of Akasaka.[20]

VII. CONCLUSION

The theory which has been proposed presents some similarities with the theory of spin-lattice relaxation in liquids[33,34] and the theory of spin-rotational relaxation. The methods here developed can be applied in these two cases with only few modifications. As a matter of fact, the axes of quantization of orbitals in a liquid have no preferential direction and thus it is necessary to average the relaxation probability over all orientations.

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[22] $\tilde{V}_c^{(1)}\epsilon$ is necessary to produce the modulation, and $\beta\vec{\mathrm{L}}\cdot\vec{\mathrm{H}}$ to give with $\lambda\vec{\mathrm{L}}\cdot\vec{\mathrm{S}}$ a g-tensor anisotropy.

[23] If we had to study the Raman process, this expansion should be to second order.

[24] This should be a good approximation, when the other levels are far enough to give a negligible contribution.

[25] Some aspects of this theory using a semiclassical formulation have been given in previous papers (Refs. 12, 13).

[26] We can better see in this formulation that the spin Zeeman term does not play a role in the relaxation process since it cannot be expressed as a function of time, the spin being quantized by the external magnetic field.

[27] In this formulation, the modulation of orientation (which is a consequence of the crystalline potential modulation) is included in the magnetic operators.

[28] The study of the Raman process is quite similar, but it will be necessary to expand θ and φ as Taylor series to second order, and to take M and $\tilde{M}$ as second-order perturbations.

[29] This is in accordance with the results given in Sec. IV regarding the role of the spin Zeeman effect.

[30] This expression is exactly the same as expression (25) when replacing $\tilde{\theta}$ by $(V_c^{(1)}\epsilon_{xz}/\Delta)\cos 2\theta_m$.

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PHYSICAL REVIEW B VOLUME 1, NUMBER 11 1 JUNE 1970

Theoretical and Experimental Investigation of Photoemission in the Region of Periodic Schottky Deviations

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The existence of deviation from the photoelectric Schottky line has been investigated for metals theoretically, and the experimental evidence for this deviation has been obtained for tungsten and molybdenum. A theoretical equation is derived based on a modified model which contains a classical image force and exchange and correlation forces. The theoretical solution indicates that the amplitude is inversely proportional to the frequency of the light source, whereas the phase or the period is found to be independent of the frequency of the light source. The experiments involved measuring the photoelectric emission current of tungsten and molybdenum as a function of electric field. Results were obtained for two different frequencies of light source for each sample. The periodic deviation from the Schottky line was observed clearly from a number of runs. A comparison of the experimental results with the theoretical prediction has been made. The agreement in the amplitude and the phase between them is very good.

I. INTRODUCTION

The periodic deviations from the Schottky line in thermionic emission were explained[1-6] as due to a periodic dependency of the transmission coefficient upon the intensity of the applied field. This periodic behavior of the transmission coefficient was interpreted as the result of interference of the electron waves reflected from the potential barrier at the surface of the metal. Since the same potential barrier is used in the theory of the surface photoelectric effect, and since the transmission coefficient enters the expression for the photocurrent in the same way, a periodic dependence of the photocurrent on the applied field, similar to the dependence of the thermionic current, is to be expected. Guth and Mullin[7] and Juenker[4] derived the periodic terms for photocurrent based on the potential barriers used for their thermionic-emission studies. A comparison between their results and the experimental data has not been available. However, since both the expressions for the thermionic periodic deviation from the Schottky line derived by Guth and Mullin[1,2] and by Juenker[4] fail to agree with the thermionic experimental results[8-14] the accuracy of their results on photoelectric emission presented a great suspicion which initiated the present work.

A modified potential barrier, which has been used to derive the periodic deviation from the Schottky line for thermionic emission,[15] and, which was found to be in excellent agreement with the experimental data, is used in this paper to derive the periodic deviation from the Schottky line for photoelectric emission. In view of the result of the theoretical derivation, it is found that the effect should be most easily observable for frequencies very near the threshold, for then the fraction of the current due to the periodic term has its largest value.

An experimental setup for photoelectric emission was built, since experimental data on photoelectric periodic deviations are not yet available in the quantity[16,17] which makes possible analysis of the counter part thermionic results. The agreement between the present theory and the present experimental results is very good.

II. PHOTOELECTRIC EMISSION FROM METALS

A periodic dependence of photoelectric emission on an applied field is expected to be from two parts: (i) for electrons with energies W and absorbing a photon $h\nu$ such that (for notation, see Ref. 15)

$$W + h\nu \geqslant V^{0\prime} \quad ,$$