sites, respectively. The S_3 resonance is due to a Si^{29} atom in the 2 nn shell.

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Spin-Lattice Relaxation in a Γ_8 Quartet: Er^{3+} in MgO

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The orbit-lattice Hamiltonian for rare-earth ions is obtained using a new approach in which it is not necessary to calculate the normal modes of the cluster consisting of the central ion and its first neighbors. The determination of the parameters describing the first-order orbit-lattice coupling is greatly simplified, whatever the environment. The problem of relaxation of a Γ_8 ground quartet is then studied. The equations of evolution of the populations are solved for one-phonon and two-phonon processes, and the relaxation times are calculated. It is shown that, under certain initial conditions, two relaxation times are sufficient. The angular variation for the one-phonon process is established. The calculations are greatly simplified by noting relations between matrix elements which were obtained from local symmetry and time-reversal considerations. The experimental results on $MgO:Er^{3+}$ verify the existence of two relaxation times and confirm their predicted angular variation. The discrepancy (a factor of 4) between experimental and theoretical values is discussed.

I. INTRODUCTION

THERE are some cases in which the splitting of the ground term of a rare-earth ion by the cubic-crystalline field results in a quartet as the ground state. This quartet, which can appear only in Kramers ions, is associated with the Γ_8 representation of the O_h group. Bleaney[1] and Ayant *et al.*[2] have developed the theory of these quartets. EPR has shown their existence and, among them, the $MgO:Er^{3+}$ system has been studied in great detail.[3,4] It is of interest to pursue this work by studying the spin-phonon coupling in this system.

Much attention has been devoted to the theoretical and experimental study of spin-phonon coupling in rare-earth ions.[5–11] But the special case of Γ_8 has never been considered theoretically,[12] and we know of only one experiment in which an attempt was made to measure the relaxation time, that of Bierig *et al.*[13] on $CaF_2:Dy^{3+}$. In their case, the relaxation time was too short to be observed. Dobrov[14] tried to measure the spin-phonon coupling by acoustic resonance, but his results were not fully explained. We shall see that the behavior of $MgO:Er^{3+}$ is, on the contrary, well understood.

In Sec. II of this paper, we deduce the orbit-lattice Hamiltonian expression, using a new approach, and we show that, for direct and Orbach processes, it is not necessary to consider only the cluster consisting of the ion and its first neighbors. We arrive at the same formal result as Orbach but with a more general meaning for the parameters describing the coupling. In addition, the calculation of these parameters for each particular case is greatly simplified, as we indicate in the Appendix. In Secs. III and IV, we give the outline of the calculation of the relaxation times due to the direct process for a Γ_8 quartet, with application to the case of $MgO:Er^{3+}$. The full use of symmetry considerations enables us to find relations between matrix elements and to show that

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they can all be deduced from usual tables for matrix elements. The solution of the equations of evolution for populations indicates that, with our experimental conditions, two relaxation times are sufficient to describe the return to equilibrium at low temperatures. In Sec. V, we give the experimental methods, and the results of measurements are compared with the theoretical predictions.

II. ORBIT-LATTICE HAMILTONIAN

A. Discussion of Approximations

To obtain the Hamiltonian describing the coupling between the magnetic moment of the ion and the crystalline vibrations, called by Orbach the orbit-lattice Hamiltonian, a number of approximations have been made by Van Vleck,[15] which have since been generally accepted. We shall consider two of them: (A) The ion is coupled only to its first neighbors; (B) the wavelength of the active crystalline vibrations is much greater than the interatomic separation. For the direct process and, in most cases, for the Orbach process, the approximation (B) is valid. Then, near the ion, the relative displacements of the neighbors are uniform and can be described by the tensor σ_{uv}, such that

$$\Delta r_u = r_u - r_u{}^0 = \sum_v \sigma_{uv} r_v{}^0 ,$$

or

$$\sigma_{uv} = \frac{\partial \Delta r_u}{\partial r_v{}^0}, \quad (u, v = x, y, z) \tag{1}$$

where r_u are the coordinates of the ion ($r_u{}^0$ the equilibrium values) and Δr_u are the displacement components.

The nine Cartesian components of σ_{uv} can be linearly combined to give nine new components belonging to the irreducible representations of the rotation group: $\mathfrak{D}_0$, $\mathfrak{D}_1$, $\mathfrak{D}_2$ because $\mathfrak{D}_1 \times \mathfrak{D}_1 = \mathfrak{D}_0 + \mathfrak{D}_1 + \mathfrak{D}_2$. To take into account the symmetry of the environment, it is better to use new linear combinations which belong to the irreducible representations of the group of local symmetry. $\sigma(\Gamma_\alpha,\beta)$ will denote the linear combination which transforms like the βth component of the representation Γ_α. The explicit form can be obtained easily for each group.

In the O_h group, $\mathfrak{D}_0 + \mathfrak{D}_1 + \mathfrak{D}_2$ reduces to $\Gamma_{1g} + \Gamma_{3g} + \Gamma_{4g} + \Gamma_{5g}$. We point out that, for $\Gamma_\alpha = \Gamma_{1g}$, Γ_{3g}, Γ_{5g}, the $\sigma(\Gamma_\alpha,\beta)$ are identical to the equivalent linear combinations of the Cartesian components of the strain tensor ϵ_{ij}, that is to say: $\sigma(\Gamma_\alpha,\beta) = \epsilon(\Gamma_\alpha,\beta)$. The ion displacements described by the $\sigma(\Gamma_{4g},\beta)$ are identical to those resulting from infinitesimal rotations of the neighborhood of the paramagnetic ion. The explicit forms of the $\sigma(\Gamma_\alpha,\beta)$ are quoted in the Appendix.

We shall see that, with such a description, approximation (A) is superflous, and that it is possible to take into account the interaction between the central ion and all the ions not too far away (the critical distance being the wavelength of the vibration).

In this paper, we adopt the approximation (B) and we suppose, in addition, that: (C) the substitution of a lattice cation by a paramagnetic ion does not modify the lattice parameter (see Sec. III); (D) the crystalline vibrations can be described by the Debye model; (E) the concentration of paramagnetic ions is small and the dipolar coupling is negligible. Though approximations (B) and (D) are not good for the Raman process, we shall use them to obtain an order of magnitude for the relaxation time.

B. Derivation of Orbit-Lattice Hamiltonian

We start from the expansion of the crystalline field in terms of spherical harmonics:

$$V = \sum_{l,m,0} A_{lm} r_0{}^l Y_l{}^m(\theta_0,\varphi_0) , \tag{2}$$

where the sum $\sum_0$ is over the paramagnetic electrons of coordinates (r_0,θ_0,φ_0). In this expansion, only the A_{lm} terms depend on the position of the neighboring ions.

As the lattice vibrations have small amplitude, the displacements of the ions are small. We can then expand the energy (2) in terms of the components of the tensor σ[16]

$$V = V_{\mathrm{st}} + \sum_{\alpha,\beta} \left[\frac{\partial V}{\partial \sigma(\Gamma_\alpha,\beta)} \right]_{\mathrm{eq}} \sigma(\Gamma_\alpha,\beta) + \text{second-order terms}. \tag{3}$$

V_{st} is the static energy. The derivative must be evaluated with the equilibrium value of the neighbor positions.

By rearranging the terms in Eq. (3), we get, for the first-order term,

$$V_{\mathrm{OL}} = \sum_{\substack{l=2,4,6;\\ 0;\alpha,\beta,a}} V_0(\Gamma_\alpha,l,a) C_0(\Gamma_\alpha{}^*,l,a,\beta) \sigma(\Gamma_\alpha,\beta) . \tag{4}$$

Using the Stevens's equivalent operators[17], we obtain the orbit-lattice Hamiltonian

$$V_{\mathrm{OL}} = \sum_{l,a,\alpha,\beta} V(\Gamma_\alpha,l,a) s_l O(\Gamma_\alpha{}^*,l,a,\beta) \sigma(\Gamma_\alpha,\beta) . \tag{5}$$

In Eqs. (4) and (5), the $C_0(\Gamma_\alpha,l,a,\beta)$ are, for each electron, the linear combination of spherical harmonics[18] of order l belonging to the βth component of the representation Γ_α, and $O(\Gamma_\alpha,l,a,\beta)$ is the associated equivalent operator. The index a distinguishes between two groups of linear combinations belonging to the same

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representation; s_l is the appropriate Stevens's multiplicative factor ($s_l=\alpha$, β, γ for $l=2$, 4, 6 in the Stevens notation). The appropriate linear combinations can be obtained, for the more common groups, from the tables given by Griffith.[19] The $V(\Gamma_\alpha,\beta,a)$ are the "parameters" which remain when all the symmetry properties are used. Their number is then fixed for a given symmetry group, whatever the surrounding and the number of normal modes of the cluster considered.

In the case of the O_h group, there are 11 coefficients $V(\Gamma_\alpha,l,a)$. That number is frequently reduced to 7 by suppressing the Γ_{1g} and Γ_{4g} terms.[14,20] It is possible to disregard the Γ_{1g} terms as soon as the nearest multiplet which belongs to the same representation as the ground multiplet is far away: such a situation is commonly encountered. For the Γ_{4g} terms, one can only point out that they are ineffective inside a multiplet which belongs to a given representation Γ_α because neither the symmetrical product $(\Gamma_\alpha\times\Gamma_\alpha)$ for a non-Kramers ion nor the antisymmetrical product $\{\Gamma_\alpha\times\Gamma_\alpha\}$ for a Kramers ion contain the Γ_{4g} representation.[21] But, when transitions between various multiplets are of importance, the Γ_{4g} terms have to be included, as they must be in the second-order terms of Eq. (3).[22]

We can, thus, rewrite Eq. (5), for the case of O_h symmetry, as

$$V_{\mathrm{OL}}=\sum_{\substack{l=2,4,6a,6b\\ \alpha=1g,3g,4g,5g;\beta}} V(\Gamma_\alpha,l)s_lO(\Gamma_\alpha{}^*,l,\beta)\sigma(\Gamma_\alpha,\beta). \quad (6)$$

Some of the $C(\Gamma_\alpha,l,\beta)$ have been quoted in Ref. 20. The others can easily be deduced from the tables of Ref. 19, taking the same convention for the basis of the representations as that used for the $\sigma(\Gamma_\alpha,\beta)$ quoted in the Appendix.

The last step is to express the σ_{uv} in terms of the lattice normal modes. For a Bravais lattice, or, for other lattices, counting only acoustical modes [approximation (D)], one has

$$\sigma_{uv}=i\sum_p\left(\frac{\hbar}{2M\omega_p}\right)^{1/2}\Phi_u{}^pk_v{}^p(a_p-a_p{}^\dagger),$$

where ω_p, $k_v{}^p$, $\Phi_u{}^p$, a_p, and $a_p{}^\dagger$ are, respectively, the angular frequency, the wave-vector components, the polarization components, the annihilation operator, and the creation operator of the mode p. The expressions for $\sigma(\Gamma_\alpha,\beta)$ can be easily deduced.

In the calculation of the relaxation time, we shall need the average value of the strain-matrix elements for all polarizations and propagation directions of the modes of a given frequency. We give below the result of this averaging along with the orthogonality properties[15]:

$$|\langle n_p|\sigma(\Gamma_\alpha,\beta)|n_p+1\rangle\langle n_p+1|\sigma^\dagger(\Gamma_{\alpha'},\beta')|n_p\rangle|_{\mathrm{av}}$$
$$=\delta_{\alpha\alpha'}\delta_{\beta\beta'}\frac{\hbar\omega(N+1)}{12Mv_m{}^2}.$$

In this equation, v_m is an average velocity of sound. For $\alpha=3g$ and $5g$, v_m is defined by

$$(1/v_m{}^2)=(6/5)(1/3v_l{}^2+1/2v_t{}^2),$$

where v_l and v_t are the velocities of longitudinal and transversal modes.

For $\alpha=4g$, v_m is simply v_t because longitudinal modes do not induce displacements associated to be $\sigma(\Gamma_{4g},\beta)$, and for $\alpha=1g$, v_m is simply v_l.

N, the mean number of quanta in a mode of frequency ω at temperature T, is given by

$$N=1/(e^{\hbar\omega/kT}-1).$$

In conclusion, Eq. (6) is formally identical with that deduced from considerations of the normal modes of the cluster.[14,20] But, with our presentation, the meaning of the $V(\Gamma_\alpha,l,a)$ is more general. In addition, we have obtained Eq. (6) without taking into account the details of the neighborhood of the ion. Of course, the expression of the $V(\Gamma_\alpha,l,a)$ depends on the actual surroundings and can be obtained easily with our method for each particular case. We give, in the Appendix, the general outlines of the calculation within the approximation of point charges.

It is clear that the method can be extended to any symmetry group. The number of parameters (243 in the case of no symmetry at all) is easily determined in each case, and, by the method shown in the Appendix, one may simplify considerably the calculation of these parameters.

Finally, we want to point out that the parameters introduced fully describe the coupling of the ion with the lattice. They are not "effective parameters," as those introduced in the dynamic-spin Hamiltonian, and it is for this reason that their number is so great. We shall see, in Sec. III, that two specific linear combinations of them are sufficient to describe the *direct process* in a Γ_8 quartet. In other terms, two phenomenological parameters should be sufficient.

III. RELAXATION IN Γ_8 QUARTET

We shall now apply the results of Sec. II to the case in which the ground state of the rare-earth ion is a Γ_8 quartet. A static magnetic field lifts the degeneracy, and the four levels a, b, c, and d have energies such that (Fig. 1) $E_a=-E_b$ and $E_c=-E_d$. The eigenstates $|a\rangle$ and $|b\rangle$ are Kramers conjugate, as also are $|c\rangle$ and $|d\rangle$.

In addition to the approximations indicated in Sec. II, we shall suppose that the quadratic Zeeman effect is negligible.

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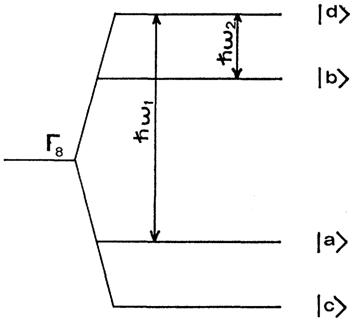

FIG. 1. Zeeman splitting of a Γ_8 quartet.

First, we consider the one-phonon process. We calculate the relaxation times and determine their variation with the magnetic-field orientation. We then solve the equations of evolution for the two-phonon processes in the range of temperature where these processes dominate.

A. Direct Process

The probability per unit time for a spin to go from the state $|b\rangle$ to the state $|a\rangle$, emitting a phonon of energy $\hbar\omega=(E_b-E_a)$, is[21]

$$W_{b\to a}=(1/4\pi\rho v^5\hbar)[(E_b-E_a)/\hbar]^3\Delta_{ab}^2(N+1)\,,$$

where

$$\Delta_{ab}^2=\sum_{\alpha,\beta}|\sum_l V(\Gamma_\alpha,l)s_l\langle a|O(\Gamma_\alpha,l,\beta)|b\rangle|^2$$

and ρ is the density of the crystal and v a mean velocity defined by

$$1/v^5=(6/5)(1/3v_l^5+1/2v_t^5)\,.$$

The probability for the reverse process is

$$W_{a\to b}=\frac{1}{4\pi\rho v^5\hbar}\left(\frac{E_b-E_a}{\hbar}\right)^3\Delta_{ab}^2N\,.$$

In the case of systems with an odd number of electrons, the interaction Hamiltonian, which is an even operator with respect to time reversal, has zero-matrix elements between two Kramers conjugate states

$$W_{ab}=W_{cd}=0\,.$$

Moreover,

$$|\langle a,n+1|V_{\mathrm{OL}}|d,n\rangle|=|\langle b,n|V_{\mathrm{OL}}|c,n+1\rangle|\,,$$
$$|\langle a,n|V_{\mathrm{OL}}|c,n+1\rangle|=|\langle b,n+1|V_{\mathrm{OL}}|d,n\rangle|\,.$$

If p and P denote the probabilities W_{db} and W_{da}, we have

$$p=W_{db}=W_{ac}\,,\quad P=W_{da}=W_{bc}\,;$$
$$W_{bd}=W_{ca}=pe^{-(E_d-E_b)/kT}=pe^{-\hbar\omega_2/kT}\,,$$
$$W_{ad}=W_{cb}=Pe^{-(E_d-E_a)/kT}=Pe^{-\hbar\omega_1/kT}\,.$$

The equations of evolution for the populations N_a, N_b, N_c, and N_d of the four levels can be written

$$\frac{d\mathbf{N}}{dt}=G\mathbf{N}\,,\qquad(7)$$

where $\mathbf{N}$ is the R^4 vector with components N_a, N_b, N_c, and N_d, and G is the operator whose associated matrix A is

$$A=\left|\begin{array}{cccc} -p-Pe^{-\hbar\omega_1/kT} & 0 & pe^{-\hbar\omega_2/kT} & P \\ 0 & -P-pe^{-\hbar\omega_2/kT} & Pe^{-\hbar\omega_1/kT} & p \\ p & P & -pe^{-\hbar\omega_2/kT}-Pe^{-\hbar\omega_1/kT} & 0 \\ Pe^{-\hbar\omega_1/kT} & pe^{-\hbar\omega_2/kT} & 0 & -P-p \end{array}\right|\,.$$

The operator G is not Hermitian. The roots of its secular equation are

$$r_1=0\,,$$
$$r_2=-p(1+e^{-\hbar\omega_2/kT})-P(1+e^{-\hbar\omega_1/kT})\,,$$
$$r_3=-P(1+e^{-\hbar\omega_1/kT})\,,$$
$$r_4=-p(1+e^{-\hbar\omega_2/kT})\,.$$

The eigenvalues are all different. It is then possible to choose a basis of R^4 which diagonalizes A. In this new basis, the differential equation (7) is easily integrated. If the equilibrium values of the populations are denoted by $(N_a)_{t=\infty}$ $(N_b)_{t=\infty}\cdots$, then the solution of (7) may be written as

$$N_a=(N_a)_{t=\infty}+C_2e^{r_2t}+C_3e^{-\hbar\omega_2/2kT}e^{r_3t}+C_4e^{\hbar\omega_1/2kT}e^{r_4t}\,,$$
$$N_b=(N_b)_{t=\infty}+C_2e^{r_2t}-C_3e^{\hbar\omega_2/2kT}e^{r_3t}-C_4e^{-\hbar\omega_1/2kT}e^{r_4t}\,,$$
$$N_c=(N_c)_{t=\infty}-C_2e^{r_2t}+C_3e^{\hbar\omega_2/2kT}e^{r_3t}-C_4e^{\hbar\omega_1/2kT}e^{r_4t}\,,$$
$$N_d=(N_d)_{t=\infty}-C_2e^{r_2t}-C_3e^{-\hbar\omega_2/2kT}e^{r_3t}+C_4e^{-\hbar\omega_1/2kT}e^{r_4t}\,,$$

where C_2, C_3, and C_4 are constants which depend on the initial conditions. Let us write

$$\lambda=2C_3\cosh(\hbar\omega_2/2kT)\,,$$

and

$$\mu=2C_4\cosh(\hbar\omega_1/2kT)\,.$$

We then have

$$N_a-N_b=(N_a-N_b)_{t=\infty}+\lambda e^{r_3t}+\mu e^{r_4t}\,,$$
$$N_c-N_d=(N_c-N_d)_{t=\infty}+\lambda e^{r_3t}-\mu e^{r_4t}\,,$$

from which

$$\lambda=\tfrac{1}{2}(N_a-N_b+N_c-N_d)_{t=0}-\tfrac{1}{2}(N_a-N_b+N_c-N_d)_{t=\infty}\,,$$
$$\mu=\tfrac{1}{2}(N_a-N_b-N_c+N_d)_{t=0}-\tfrac{1}{2}(N_a-N_b-N_c+N_d)_{t=\infty}\,.$$

In our experimental conditions, we observe the time variation of N_a-N_b. We shall suppose that the perturbation is applied for a time sufficiently short to modify only the populations of levels a and b and to leave the c and d levels unchanged.

We then obtain

$$(N_a-N_b)_t-(N_a-N_b)_{t=\infty} = -(N_a-N_b)_{t=\infty}(e^{-t/\tau_1{}^D}+e^{-t/\tau_2{}^D}),$$

when the populations are initially inverted, and

$$(N_a-N_b)_t-(N_a-N_b)_{t=\infty} = -\tfrac{1}{2}(N_a-N_b)_{t=\infty}(e^{-t/\tau_1{}^D}+e^{-t/\tau_2{}^D}),$$

when the populations are initially made equal by saturation. The relaxation times $\tau_1{}^D$ and $\tau_2{}^D$ are given by

$$1/\tau_1{}^D=-r_3=(1/4\pi\rho v^5\hbar) \times[(E_d-E_a)/\hbar]^3\Delta_{ad}{}^2 \coth[(E_d-E_a)2kT],$$

and

$$1/\tau_2{}^D=-r_4=(1/4\pi\rho v^5\hbar) \times[(E_d-E_b)/\hbar]^3\Delta_{bd}{}^2 \coth[(E_d-E_b)/2kT].$$

Since, generally,

$$(E_d-E_a)/2kT\ll 1,$$

we can write to a good approximation

$$\begin{aligned} 1/\tau_1{}^D&=(kT/2\pi\rho v^5\hbar^2)[(E_d-E_a)/\hbar]^2\Delta_{ad}{}^2, \\ 1/\tau_2{}^D&=(kT/2\pi\rho v^5\hbar^2)[(E_d-E_b)/\hbar]^2\Delta_{bd}{}^2. \end{aligned} \tag{8}$$

For a fixed orientation of the magnetic field, $1/\tau_1{}^D$ and $1/\tau_2{}^D$ are proportional to H^2 (in the case of Kramers systems with a Γ_6 or Γ_7 ground level, $\tau^D \propto T^{-1}H^{-4}$ for the direct process).

B. Calculation of Matrix Elements of Orbit-Lattice Hamiltonian

Let us choose, for the frame of reference, the 3 fourfold axes of the cube. When $\mathbf{H}$ is parallel to $0z$, the eigenstates of the Zeeman sublevels, which we shall denote by $\|M\rangle$, are given by

$$\|\pm\tfrac{3}{2}\rangle=\sum_{M_J}\alpha_{M_J}|J,\pm M_J\rangle \quad \text{with } M_J=\pm\tfrac{3}{2} \bmod 4,$$

$$\|\pm\tfrac{1}{2}\rangle=\sum_{M_J}\alpha_{M_J}|J,\pm M_J\rangle \quad \text{with } M_J=\pm\tfrac{1}{2} \bmod 4.$$

These four particular eigenstates will be chosen as the basis for the subspace associated with the Γ_8 representation.

We obtain, by application of the time-reversal operation,

$$\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|-\tfrac{1}{2}\rangle=\langle\tfrac{3}{2}\|V_{\mathrm{OL}}\|-\tfrac{3}{2}\rangle=0,$$

$$\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle=-\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}\|-\tfrac{3}{2}\rangle^\dagger,$$

$$\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|-\tfrac{3}{2}\rangle=\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle^\dagger,$$

whese the dagger denotes Hermitian conjugate (because these matrix elements are, in fact, lattice operators).

From the selection-rule theorem,

$$\langle\tfrac{1}{2}\|O_l{}^m\|\tfrac{3}{2}\rangle\neq 0 \quad \text{only if } m=-5,\,-1,\,+3,$$

$$\langle-\tfrac{1}{2}\|O_l{}^m\|\tfrac{3}{2}\rangle\neq 0 \quad \text{only if } m=\pm 2,\,\pm 6.$$

We then deduce

$$\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle=\Big[\sum_{l=2,4,6a,6b}\langle\tfrac{1}{2}\|O(\Gamma_{5g},l,1)\|\tfrac{3}{2}\rangle \times s_lV(\Gamma_{5g},l)\Big]\epsilon(\Gamma_{5g},1) =A(\Gamma_{5g},1)\epsilon(\Gamma_{5g},1),$$

$$\langle\tfrac{3}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle=\Big[\sum_l\langle\tfrac{3}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{3}{2}\rangle s_lV(\Gamma_{3g},l)\Big]\epsilon(\Gamma_{3g},\theta) =A(\Gamma_{3g},\theta)\epsilon(\Gamma_{3g},\theta),$$

$$\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{1}{2}\rangle=\Big[\sum_l\langle\tfrac{1}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{1}{2}\rangle s_lV(\Gamma_{3g},l)\Big]\epsilon(\Gamma_{3g},\theta) =A'(\Gamma_{3g},\theta)\epsilon(\Gamma_{3g},\theta),$$

and

$$\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle=\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}(\Gamma_{3g})\|\tfrac{3}{2}\rangle+\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}(\Gamma_{5g})\|\tfrac{3}{2}\rangle,$$

where

$$\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}(\Gamma_{3g})\|\tfrac{3}{2}\rangle=\Big[\sum_l\langle-\tfrac{1}{2}\|O(\Gamma_{3g},l,\xi)\|\tfrac{3}{2}\rangle \times s_lV(\Gamma_{3g},l)\Big]\epsilon(\Gamma_{3g},\xi) =A(\Gamma_{3g},\xi)\epsilon(\Gamma_{3g},\xi),$$

and

$$\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}(\Gamma_{5g})\|\tfrac{3}{2}\rangle=\Big[\sum_l\langle-\tfrac{1}{2}\|O(\Gamma_{5g},l,0)\|\tfrac{3}{2}\rangle \times s_lV(\Gamma_{5g},l)\Big]\epsilon(\Gamma_{5g},0) =A(\Gamma_{5g},0)\epsilon(\Gamma_{5g},0).$$

The computation of $A(\Gamma_{5g},1)$ and $A(\Gamma_{5g},\,-1)$ requires the knowledge of matrix elements which are not tabulated. We show, however, that these are simply related to $A(\Gamma_{5g},0)$, which is easily evaluated.

The starting point is the invariance of any matrix element under any operation of the group. We shall, for instance, use the invariance of $\langle\tfrac{1}{2}\|O(\Gamma_{5g},l,1)\|\tfrac{3}{2}\rangle$ under the rotation $\mathbf{R}(0x,\pi/2)$. As $\mathfrak{D}_{3/2}=\Gamma_{8g}$, we have, from the explicit expression of the matrix $\mathfrak{D}_{3/2}(0x,\pi/2)$,

$$R\|\tfrac{3}{2}\rangle=\frac{1}{2\sqrt{2}}\|\tfrac{3}{2}\rangle-\frac{i\sqrt{3}}{2\sqrt{2}}\|\tfrac{1}{2}\rangle-\frac{\sqrt{3}}{2\sqrt{2}}\|-\tfrac{1}{2}\rangle+\frac{i}{2\sqrt{2}}\|-\tfrac{3}{2}\rangle,$$

$$R\|\tfrac{1}{2}\rangle=-\frac{i\sqrt{3}}{2\sqrt{2}}\|\tfrac{3}{2}\rangle-\frac{1}{2\sqrt{2}}\|\tfrac{1}{2}\rangle-\frac{i}{2\sqrt{2}}\|-\tfrac{1}{2}\rangle-\frac{\sqrt{3}}{2\sqrt{2}}\|-\tfrac{3}{2}\rangle.$$

From $\Gamma_{5g}=\Gamma_{4g}\times\Gamma_{2g}$, and from $\mathfrak{D}_1=\Gamma_{4g}$, we deduce[23]

$$R[O(\Gamma_{5g},l,1)]=-\tfrac{1}{2}O(\Gamma_{5g},l,1) +\frac{i}{\sqrt{2}}O(\Gamma_{5g},l,0)+\tfrac{1}{2}O(\Gamma_{5g},\,l,\,-1).$$

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[23] These formulas for the transformation of operators and wave functions under $\mathbf{R}(Ox,\pi/2)$ are also given in Ref. 19.

The invariance of $\langle\frac{1}{2}\|O(\Gamma_{5g},l,1)\|\frac{3}{2}\rangle$ leads to

$$\langle\tfrac{1}{2}\|O(\Gamma_{5g},l,1)\|\tfrac{3}{2}\rangle=-\sqrt{2}\langle-\tfrac{1}{2}\|O(\Gamma_{5g},l,0)\|\tfrac{3}{2}\rangle,$$

and

$$A(\Gamma_{5g},1)=-\sqrt{2}A(\Gamma_{5g},0). \tag{9}$$

Similarily, one can relate $A(\Gamma_{3g},\theta)$, $A'(\Gamma_{3g},\theta)$, and $A(\Gamma_{3g},\xi)$. From

$$R[O(\Gamma_{3g},l,\xi)]=\tfrac{1}{2}O(\Gamma_{3g},l,\xi)-(\sqrt{3}/2)O(\Gamma_{3g},l,\theta),$$

and from the invariance of $\langle\frac{1}{2}\|O(\Gamma_{3g},l,\xi)\|\frac{1}{2}\rangle=0$ and $\langle\frac{3}{2}\|O(\Gamma_{3g},l,\xi)\|\frac{3}{2}\rangle=0$, we deduce

$$\langle\tfrac{3}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{3}{2}\rangle+3\langle\tfrac{1}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{1}{2}\rangle +2\langle-\tfrac{1}{2}\|O(\Gamma_{3g},l,\xi)\|\tfrac{3}{2}\rangle=0,$$

and

$$3\langle\tfrac{3}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{3}{2}\rangle+\langle\tfrac{1}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{1}{2}\rangle -2\langle-\tfrac{1}{2}\|O(\Gamma_{3g},l,\xi)\|\tfrac{3}{2}\rangle=0.$$

From these relations, we obtain

$$\langle\tfrac{3}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{3}{2}\rangle=-\langle\tfrac{1}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{1}{2}\rangle,$$
$$\langle\tfrac{3}{2}\|O(\Gamma_{3g},l,\theta)\|\tfrac{3}{2}\rangle=-\langle\tfrac{1}{2}\|O(\Gamma_{3g},l,\xi)\|\tfrac{3}{2}\rangle,$$

and

$$\begin{aligned}A'(\Gamma_{3g},\theta)&=A(\Gamma_{3g},\theta),\\ A(\Gamma_{3g},\xi)&=A(\Gamma_{3g},\theta).\end{aligned} \tag{10}$$

In conclusion, we have shown that the only matrix elements we have to calculate are those included in $A(\Gamma_{3g},\theta)$ and $A(\Gamma_{5g},O)$.

C. Dependence of Relaxation Times on Orientation of Magnetic Field

The diagonalization of the Zeeman Hamiltonian gives the eigenstates $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$ as linear combinations of $\|M\rangle$ states. Let us write

$$|d\rangle=d_1\|\tfrac{3}{2}\rangle+d_2\|\tfrac{1}{2}\rangle+d_3\|-\tfrac{1}{2}\rangle+d_4\|-\tfrac{3}{2}\rangle,$$
$$|b\rangle=b_1\|\tfrac{3}{2}\rangle+b_2\|\tfrac{1}{2}\rangle+b_3\|-\tfrac{1}{2}\rangle+b_4\|-\tfrac{3}{2}\rangle,$$
$$\pm|a\rangle=-b_4{}^*\|\tfrac{3}{2}\rangle+b_3{}^*\|\tfrac{1}{2}\rangle-b_2{}^*\|-\tfrac{1}{2}\rangle+b_1{}^*\|-\tfrac{3}{2}\rangle,$$
$$\pm|c\rangle=-d_4{}^*\|\tfrac{3}{2}\rangle+d_3{}^*\|\tfrac{1}{2}\rangle-d_2{}^*\|-\tfrac{1}{2}\rangle+d_1{}^*\|-\tfrac{3}{2}\rangle.$$

The two latter states are deduced by time-reversal operation on the former. We choose the sign plus or minus, respectively, as $j=15/2$ modulus 2, or $J=13/2$ modulus 2. The orthogonality of these vectors requires

$$b_4d_1+b_2d_3=b_3d_2+b_1d_4,$$

and

$$b_1{}^*d_1+b_2{}^*d_2+b_3{}^*d_3+b_4{}^*d_4=0.$$

Then,

$$\begin{aligned}\pm\langle a|V_{\mathrm{OL}}|d\rangle=&(-b_4d_1+b_1d_4)\langle\tfrac{3}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle\\ &+(b_3d_2-b_2d_3)\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{1}{2}\rangle\\ &+(b_3d_1-b_1d_3)\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle\\ &+(-b_4d_2+b_2d_4)\langle\tfrac{3}{2}\|V_{\mathrm{OL}}\|\tfrac{1}{2}\rangle\\ &+(-b_2d_1+b_1d_2)\langle-\tfrac{1}{2}\|V_{\mathrm{OL}}\|\tfrac{3}{2}\rangle\\ &+(-b_4d_3+b_3d_4)\langle\tfrac{1}{2}\|V_{\mathrm{OL}}\|-\tfrac{3}{2}\rangle.\end{aligned}$$

Using Eqs. (9) and (10), we obtain

$$\begin{aligned}\Delta_{ad}{}^2=&\{4|-b_4d_1+b_1d_4|^2\\ &+|-b_2d_1+b_1d_2-b_4d_3+b_3d_4|^2\}[A(\Gamma_{3g},\xi)]^2\\ &+\{2|b_3d_1-b_1d_3|^2+2|-b_4d_2+b_2d_4|^2\\ &+|-b_2d_1+b_1d_2+b_4d_3-b_3d_4|^2\}[A(\Gamma_{5g},0)]^2.\end{aligned}$$

The expression of $\Delta_{bd}{}^2$ is deduced from that of $\Delta_{ad}{}^2$ by replacing b_1, b_2, b_3, and b_4 with $b_4{}^*$, $-b_3{}^*$, $b_2{}^*$, and $-b_1{}^*$, respectively.

We can now establish the angular variation of the relaxation times in an actual case using Eq. (8), where the values of (E_d-E_a) and (E_b-E_a) can be obtained from Ref. 2. We see that, as group theory predicts, two terms, $A(\Gamma_{3g},\xi)$ and $A(\Gamma_{5g},\theta)$, are sufficient to describe the one-phonon process.

D. Two-Phonon Processes

The transition probability for the two-phonon process between the Kramer's conjugate states is not zero. The return to equilibrium after the perturbation of the populations is not so simple as it was for the direct process. With the same notations as before, the G operator of Eq. (7) has three nonzero eigenvalues, r_2, r_3, and r_4, from which we deduced the three relaxation times,

$$1/\tau_1=-r_2,\quad 1/\tau_2=-r_3,\quad 1/\tau_3=-r_4.$$

Let us consider the case in which kT is much larger than the Zeeman splitting of the Γ_8 levels. In these conditions, we find

$$\begin{aligned}1/\tau_1=&2(W_{db}+W_{da}),\\ 1/\tau_2=&W_{db}+W_{da}+W_{ba}+W_{dc}\\ &+[(W_{db}-W_{da})^2+(W_{ba}-W_{dc})^2]^{1/2},\\ 1/\tau_3=&W_{db}+W_{da}+W_{ba}+W_{dc}\\ &-[(W_{db}-W_{da})^2+(W_{ba}-W_{dc})^2]^{1/2}.\end{aligned} \tag{11}$$

The expression for the transition probabilities are given, for instance, in Ref. 5. Without going into detail, we point out that, in addition to the Orbach process, the Raman process can give three terms with different temperature dependence, due to the fact that the ground state is Γ_8. The T^9 and T^5 terms, characteristic of a Kramers ion, both appear since there exist, respectively, far-excited and near-excited (Γ_8 itself) levels.[11] The T^7 term appears because, inside the Γ_8 quartet, the transition probabilities between non-Kramers-conjugate levels are nonzero. It is clear that, in an actual case and for a given temperature range, one or two of these terms dominate and some of the transition probabilities which appear in Eq. (11) can be neglected. In Sec. IV, we shall give the results of the calculation for the case of MgO:Er^{3+}. This calculation will be also greatly simplified owing to relations analogous to (9) and (10) between matrix elements.

IV. APPLICATION TO MgO:Er^{3+}

The ground level of the $4f^{11}$ configuration of Er^{3+} is $^4I_{15/2}$. In the octahedral-crystal field of MgO, the degeneracy of this $J=15/2$ state is partially removed (Fig. 2). Lea *et al.*[24] have calculated the energies and eigenfunctions of the crystalline levels as a function of the parameter x characterizing the relative importance of the fourth- and sixth-order terms of the crystalline Hamiltonian. For $J=15/2$, the eigenfunctions of the Γ_8 ground quartet depend on the x value, because Γ_8 appears three times in the reduction of $\mathfrak{D}_{15/2}$. The effect of the magnetic field is described by two parameters called P and Q by Ayant *et al.*[2] The values deduced from the experimental spectra are given by[3]

$$P=4.927, \quad Q=1.925, \quad x=0.71.$$

From the quadratic Zeeman effect, Descamps and Merle d'Aubigné have determined the scale of the cubic-field splitting ($W=1.66$ cm^{-1}; in the Lea Leask and Wolf notation). Figure 2 gives the energies of the various levels.

The eigenstates of the Γ_8 ground quartet for the magnetic field parallel to $\langle 100\rangle$ are given by[21]

$$\|\pm\tfrac{3}{2}\rangle=\alpha_{13/2}|\mp\tfrac{13}{2}\rangle+\alpha_{5/2}|\mp\tfrac{5}{2}\rangle+\alpha_{3/2}|\pm\tfrac{3}{2}\rangle+\alpha_{11/2}|\pm\tfrac{11}{2}\rangle,$$

$$\|\pm\tfrac{1}{2}\rangle=\alpha_{15/2}|\mp\tfrac{15}{2}\rangle+\alpha_{7/2}|\mp\tfrac{7}{2}\rangle+\alpha_{1/2}|\pm\tfrac{1}{2}\rangle+\alpha_{3/2}|\pm\tfrac{9}{2}\rangle;$$

$$\alpha_{13/2}=0.0270, \qquad \alpha_{5/2}=0.1845,$$

$$\alpha_{3/2}=-0.2309, \quad \alpha_{11/2}=0.9549,$$

$$\alpha_{15/2}=0.0331, \qquad \alpha_{7/2}=0.4698,$$

$$\alpha_{1/2}=-0.4456, \quad \alpha_{9/2}=0.7613.$$

With these values and the results of Sec. III, we obtain

$$A(\Gamma_{3g},\xi)=[2.551V(\Gamma_{3g},2)+2.398V(\Gamma_{3g},4)-7.094V(\Gamma_{3g},6)]\times 10^{-2},$$

$$A(\Gamma_{5g},0)=[-4.742V(\Gamma_{5g},2)-0.913V(\Gamma_{5g},4)+5.545V(\Gamma_{5g},6,A)+8.357V(\Gamma_{5g},6,B)]\times 10^{-2}.$$

To estimate the $V(\Gamma_\alpha,la)$, we shall use the spectroscopic results. As we have seen, the quadratic Zeeman effect has given the scale of the cubic-field splitting, and the parameter x has given the ratio between fourth-order and sixth-order terms of the crystalline field. Using the point-charge contribution of the nearest neighbors only, we obtain[25]

$$\frac{ee'\langle r^4\rangle}{R^5}=-\frac{16}{7}\frac{Wx}{\beta_J F(4)},$$

and

$$\frac{R^2\langle r^4\rangle}{\langle r^6\rangle}=\frac{3}{28}\frac{F(6)}{F(4)}\frac{\gamma_J}{\beta_J}(1-|x|).$$

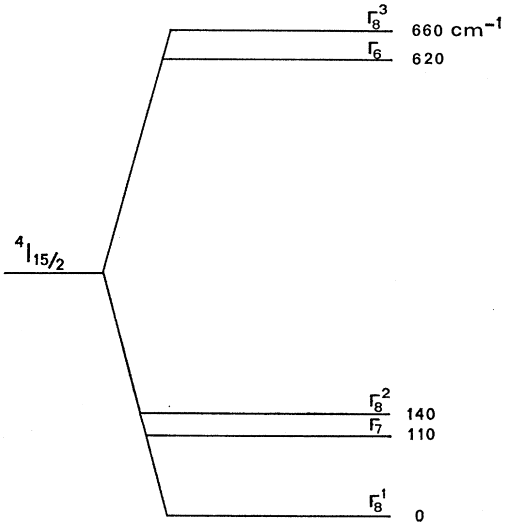

FIG. 2. Crystal-field splitting of the $^4I_{15/2}$ ground term of Er^{3+} in MgO.

With the experimental values of W and x, we deduce

$$\frac{ee'\langle r^4\rangle}{R^5}=-1010\text{ cm}^{-1} \quad\text{and}\quad \frac{ee'\langle r^6\rangle}{R^7}=-360\text{ cm}^{-1}. \tag{12}$$

These values must be compared with

$$\frac{ee'\langle r^4\rangle}{R^5}=-500\text{ cm}^{-1}, \quad \frac{ee'\langle r^6\rangle}{R^7}=-110\text{ cm}^{-1}, \tag{13}$$

obtained with $e'=-2e$, $R=2.1$ Å (the lattice parameter of pure MgO), and the values $\langle r^4\rangle=1.126a_0^4$ and $\langle r^6\rangle=3.978a_0^6$ for the free ion given by Freeman and Watson.[26]

The difference between the values (12) and (13) can be explained by several effects. First, because the ionic radius of Er^{3+} (1.04 Å) is greater than that of Mg^{2+} (0.78 Å), and because Er^{3+} has an extra charge, the value of R can be modified. The magnitude of this modification has been calculated by Borg and Ray, and the result shows that R is reduced by about 10%.[27] This correction gives a better agreement between (12) and (13). Second, the values of $\langle r^n\rangle$ in a solid can be different from the values for the free ion. It was found, for instance in $PrCl_3$, that these values are increased many times.[28] Those modifications are very sensitive to the chemical bonding and must be evaluated for each particular case.

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[24] R. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[25] If one takes into account the contribution of all neighbors until the fifth, these values are only affected by ~2% for the fourth-order terms and 6% for the sixth-order terms.

[26] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[27] M. Borg and D. K. Ray, Phys. Rev. (to be published).

[28] M. T. Hutchings and D. K. Ray, Proc. Phys. Soc. (London) **81**, 663 (1963).

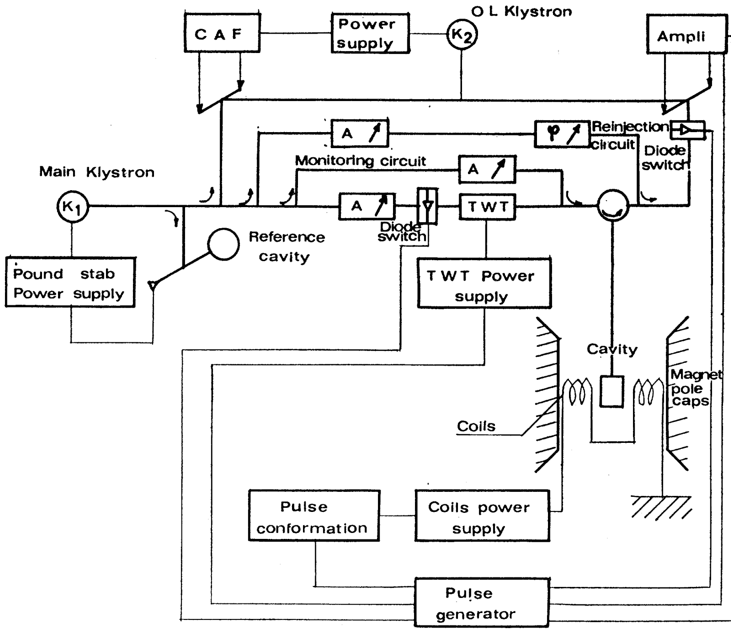

FIG. 3. Block diagram of the apparatus.

The value $ee'\langle r^2\rangle/R^3$ cannot be deduced from known experimental results. We shall use the value -2400 cm^{-1} obtained with $\langle r^2\rangle = 0.666a_0^2$,[26] $R=2.1$ Å, and a shielding coefficient $\alpha=0.5$ (see the discussion in Sec. V). With this value, and the values (11) deduced from experiments, we calculate the parameters $V(\Gamma_\alpha,l)$ taking into account all the neighbors up to the fourth (see Appendix). We obtain

$$\begin{aligned}
V(\Gamma_{1g},4) &= -1.12\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{1g},6) &= -0.335\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{3g},2) &= -1.44\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{3g},4) &= 0.861\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{3g},6) &= -0.435\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{4g},4) &= 0.708\times 10^4 \text{ cm}^{-1}, \qquad (14)\\
V(\Gamma_{4g},6) &= -0.220\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{5g},2) &= -0.960\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{5g},4) &= 0.262\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{5g},6a) &= -0.099\times 10^4 \text{ cm}^{-1},\\
V(\Gamma_{5g},6b) &= -0.290\times 10^4 \text{ cm}^{-1},
\end{aligned}$$

TABLE I. Angular variation of theoretical and adjusted values of the products $\tau_i T$ (in units of 10^{-3} sec°K).

θ	0	10	20	25	45
$(\tau_1 T)_{\text{th}}$	1.24	1.20	1.16	1.08	0.98
$(\tau_2 T)_{\text{th}}$	8.5	7.7	5.9	5.1	3.6
$(\tau_1 T)_{\text{adj}}$	0.44	0.43	0.40	0.37	0.32
$(\tau_2 T)_{\text{adj}}$	2.2	2.07	1.76	1.59	1.27

and, from these values,

$$A(\Gamma_{3g},\xi) = 150 \text{ cm}^{-1},$$
$$A(\Gamma_{5g},0) = 120 \text{ cm}^{-1}.$$

It is easy to verify that the transition probabilities between Kramers's conjugate states are negligible (they are always 10^2 smaller than the transition probabilities between non-Kramers's conjugate states) and to calculate the relaxation times with Eqs. (8) using $\rho=3.58$ and $v=6.4\times 10^5$ cm/sec. The first two rows of Table I give the results obtained with the experimental value of the resonant frequency (9100 MHz) and with the magnetic field lying in a $\{100\}$ plane at an angle θ to a $\langle 100\rangle$ direction. When $\mathbf{H}$ is parallel to $\langle 111\rangle$, we obtain

$$\tau_1 T = 0.86\times 10^{-3} \text{ sec°K},$$
$$\tau_2 T = 1.6\times 10^{-3} \text{ sec°K}.$$

We have also calculated the relaxation times due to Orbach and Raman processes taking into account the Γ_7 and the $\Gamma_8{}^2$ excited levels when $\mathbf{H}$ is parallel to $\langle 100\rangle$. For this calculation, we have not considered the quadratic terms of the orbit-lattice Hamiltonian, but we have included the linear terms which belong to Γ_{1g} and Γ_{4g}. The various matrix elements which have to be calculated are of the form

$$\begin{aligned}
\langle \Gamma_8{}^{(1)}m \| V_{\text{OL}}(\Gamma_\alpha,\beta) \| \Gamma_n,m'\rangle
&= [\lambda_2 V(\Gamma_\alpha,2)+\lambda_4 V(\Gamma_\alpha,4)+\lambda_{6a} V(\Gamma_\alpha,6a)\\
&\quad +\lambda_{6b} V(\Gamma_\alpha,6b)]\sigma(\Gamma_\alpha,\beta)\times 10^{-2}, \qquad (15)
\end{aligned}$$

where $V_{\text{OL}}(\Gamma_\alpha,\beta)$ is the part of V_{OL} corresponding to the βth component of the Γ_α representation and where $\|\Gamma_n,m'\rangle$ are the excited states. Table II gives the values of the λ_i for the various terms. These values are calculated with the following states[29]:

$$\|\Gamma_7,\pm\tfrac{1}{2}\rangle=0.6332|\mp\tfrac{13}{2}\rangle+0.5819|\mp\tfrac{5}{2}\rangle-0.4507|\pm\tfrac{3}{2}\rangle-0.2393|\pm\tfrac{11}{2}\rangle,$$

$$\|\Gamma_8{}^{(2)},\pm\tfrac{1}{2}\rangle=0.0677|\mp\tfrac{15}{2}\rangle+0.7534|\mp\tfrac{7}{2}\rangle-0.2400|\pm\tfrac{1}{2}\rangle-0.6084|\pm\tfrac{9}{2}\rangle,$$

$$\|\Gamma_8{}^{(2)},\pm\tfrac{3}{2}\rangle=0.7731|\mp\tfrac{13}{2}\rangle-0.4643|\mp\tfrac{5}{2}\rangle+0.3995|\pm\tfrac{3}{2}\rangle+0.1644|\pm\tfrac{11}{2}\rangle.$$

It is then possible, with the values given by (14), to evaluate the transition probabilities for the various two-phonon processes. We obtain

$$W_{ba}{}^{\mathrm{R}}=1.9\times10^{-9}T^9,\quad W_{dc}{}^{\mathrm{R}}=0.61\times10^{-9}T^9,$$

$$W_{da}{}^{\mathrm{R}}=4.7\times10^{-7}T^7,\quad W_{db}{}^{\mathrm{R}}=7.9\times10^{-7}T^7,$$

$$W_{ba}{}^{\mathrm{O}}=1.9\times10^9e^{-158/T}+3\times10^9e^{-202/T},$$

$$W_{dc}{}^{\mathrm{O}}=0.4\times10^9e^{-158/T}+1.5\times10^9e^{-202/T},$$

$$W_{da}{}^{\mathrm{O}}=1.5\times10^9e^{-158/T}+2.9\times10^9e^{-202/T},$$

$$W_{db}{}^{\mathrm{O}}=2.6\times10^9e^{-158/T}+4.8\times10^9e^{-202/T},$$

$$W_{ba}{}^{\mathrm{BO}}=W_{dc}{}^{\mathrm{BO}}=1.9\times10^{-4}T^5,$$

where $W_{ij}{}^{\mathrm{R}}$, $W_{ij}{}^{\mathrm{O}}$, and $W_{ij}{}^{\mathrm{BO}}$, are, respectively, the transition probabilities between the i and j states due to the Raman, Orbach, and Blume-Orbach[11] processes.

With these values and Eqs. (10), we have calculated the relaxation times associated with each process. We have found that, for temperatures below 55°K, the Orbach process is dominant and the relaxation times are of the order of $10^{10}\times e^{-158/T}$. This result indicates that the Orbach and the direct processes are of the same order of magnitude for $T\sim 11$°K.

V. EXPERIMENTS AND RESULTS

Figure 3 shows a block diagram of the experimental apparatus which was constructed by Berthier.[30] It can be used either to invert the populations by fast adiabatic passage or to saturate the transitions.

The microwave frequency was about 9100 MHz for all the measurements. The temperature of the sample was varied in the 1.3–4.2°K range and was measured by the vapour pressure at the surface of the liquid-helium bath. The crystals were obtained from Semi-Elements Inc. and are nominaly doped with 0.3% Er^{3+}. The recovery signals were nonexponential at any temperature, but they were always fitted by a sum of two exponentials with equal weight, as the theory predicted:

$$S=S_0(e^{-t/\tau_1}+e^{-t/\tau_2}),\quad(\tau_1<\tau_2).$$

The cross relaxation was ruled out because (i) the time constants of the two exponentials vary with the temperature; (ii) the shortest time constant is unaffected by a variation of the duration of the saturation, (iii) the relaxation times are short, reducing the influence of fast relaxing ion which could possibly be present; and (iv) the angular variation follows the theory very well.

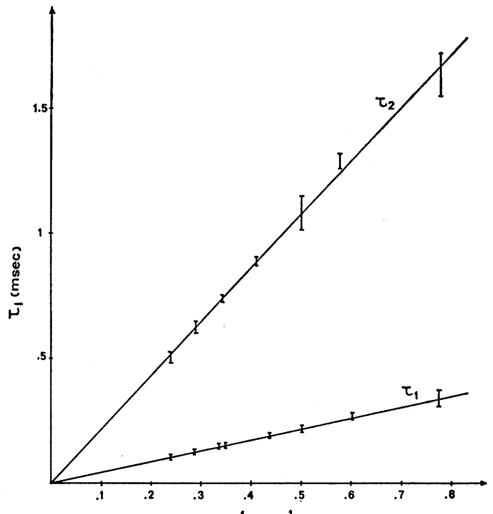

FIG. 4. Temperature dependence of the two relaxation times.

The longer relaxation time was obtained by use of the pulse-saturation technique which gives a better stability of the base line. In the tail of the recovery signal, the variation due to the first exponential is negligible and the points fall very well on a straight line on a semilog plot. The slope of this line is τ_2. The shorter time was deduced from measurements with fast adiabatic passage which gives a signal about twice as large. Just after the inversion, the points of the decay curve fall on a straight line on a semi-log plot. The value of τ_1 can easily be deduced from the slope (but is not identical to it) of this straight line and from the τ_2 value.[31]

Figure 4 shows the temperature variation of τ_1 and τ_2 when **H** is parallel to ⟨100⟩. These results are fitted by

$$\tau_2T=(2.2\pm0.1)\times10^{-3}\ \mathrm{sec°K},$$

$$\tau_1T=(0.44\pm0.04)\times10^{-3}\ \mathrm{sec°K}.$$

TABLE II. Values of the λ_i coefficients of Eq. (15).

$\Gamma_8{}^{(1)}, m$	$\Gamma_{n,m'}$	Γ_α,β	λ_2	λ_4	λ_{6a}	λ_{6b}
$\Gamma_8{}^{(1)},-\frac{1}{2}$	$\Gamma_7,\frac{1}{2}$	Γ_{3g},ξ	2.01	3.34	−1.75	0
$\Gamma_8{}^{(1)},\frac{3}{2}$	$\Gamma_7,\frac{1}{2}$	$\Gamma_{4g},0$	0	−2.03	−2.75	0
$\Gamma_8{}^{(1)},-\frac{1}{2}$	$\Gamma_7,\frac{1}{2}$	$\Gamma_{5g},0$	−4.73	4.85	2.83	5.78
$\Gamma_8{}^{(1)},\frac{3}{2}$	$\Gamma_8{}^{(2)},\frac{3}{2}$	Γ_{1g}	0	0.60	−3.68	0
$\Gamma_8{}^{(1)},\frac{3}{2}$	$\Gamma_8{}^{(2)},\frac{3}{2}$	Γ_{3g},θ	1.86	3.32	−0.55	0
$\Gamma_8{}^{(1)},\frac{3}{2}$	$\Gamma_8{}^{(2)},\frac{3}{2}$	$\Gamma_{4g},0$	0	2.36	5.98	0
$\Gamma_8{}^{(1)},\frac{1}{2}$	$\Gamma_8{}^{(2)},\frac{1}{2}$	$\Gamma_{4g},0$	0	−3.68	0.65	0
$\Gamma_8{}^{(1)},-\frac{1}{2}$	$\Gamma_8{}^{(2)},\frac{3}{2}$	$\Gamma_{5g},0$	7.61	2.05	−0.31	−9.29
$\Gamma_8{}^{(1)},\frac{3}{2}$	$\Gamma_8{}^{(2)},-\frac{1}{2}$	$\Gamma_{5g},0$	4.49	1.99	−6.71	−2.62

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[29] E. Belorizky (private communication).

[30] Y. Berthier, thesis, Faculté des Sciences, Grenoble, 1966 (unpublished).

[31] C. Jacolin, thesis, Faculté des Sciences, Grenoble, 1968 (unpublished).

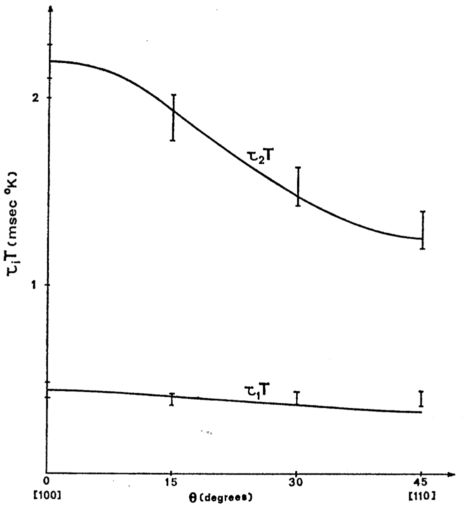

FIG. 5. Experimental angular variation of the products τ_iT. The magnetic field lies in a {1 0 0} plane and θ is the angle between **H** and ⟨1 0 0⟩. The solid lines correspond to the theoretical results, the values of the parameters $A(\Gamma_{3g},\xi)$ and $A(\Gamma_{5g},0)$ being determined from the measured values of τ_1 and τ_2 for **H** parallel to ⟨1 0 0⟩.

The angular variation of the products τ_iT when **H** lies in a {100} plane and makes an angle θ with ⟨100⟩ is shown on Fig. 5.

When **H** is parallel to ⟨111⟩, it is not possible to distinguish between τ_1 and τ_2. We can only conclude that $\tau_1T \lesssim 0.6\times10^{-3}$ sec °K and $\tau_2T \gtrsim 0.65\times10^{-3}$ sec °K.

In order to compare the theoretical and experimental angular variations, we have used the experimental values of τ_iT for **H** parallel to ⟨100⟩ to determine $A(\Gamma_{3g},\xi)$ and $A(\Gamma_{5g},0)$, and we have found

$$A(\Gamma_{5g},0)=240\pm6\ \text{cm}^{-1},$$
$$A(\Gamma_{3g},\xi)=230\pm23\ \text{cm}^{-1}.$$

We have calculated the products τ_iT for other field directions. The results are given in rows 3 and 4 of Table I and are represented by the curve on Fig. 5. For **H** parallel to ⟨111⟩, we find $\tau_1T=0.3\times10^{-3}$ sec °K and $\tau_2T=0.8\times10^{-3}$ sec °K.

The experimental results confirm some theoretical conclusions: (i) The one-phonon process is dominant in the investigated temperature range; (ii) the angular variation follows the theoretical predictions very well; and (iii) the experimental and theoretical ratios between the long- and the short-relaxation times are comparable. For **H** parallel to ⟨100⟩,

$$\left(\frac{\tau_2}{\tau_1}\right)_{\text{exp}}=5.0 \quad\text{and}\quad \left(\frac{\tau_2}{\tau_1}\right)_{\text{th}}\sim6.8.$$

The agreement between the absolute values of the relaxation times is not very good; there is a ratio of 4, with the theoretical relaxation rate smaller than the experimental one. The cross relaxation has already been ruled out as a possibility for the discrepancy. We also reject the possibility that the value of the average sound velocity (to which the theoretical results depend sensitively) is not correct: The value adopted comes from a sophisticated averaging on the 13 special directions of cubic symmetry[21,32] and must be correct. Also, we have used the static values of $ee'\langle r^n\rangle/R^{n+1}$ ($n=4$, 6) deduced from spectroscopic measurements, and it is not impossible, although highly unlikely, that the dynamic values are different.

We feel that the major part of the discrepancy probably comes from the second-order term for which we have taken $R=2.1$ Å (the unperturbed lattice value) and $\alpha=0.5$. We have already indicated that the modification of the value of R, calculated in Ref. 27, is about 10%. The value of $\alpha=0.5$ is not precise and was chosen from the results obtained by Barnes *et al.*[33] for Tm^{3+} (the neighbor of Er in the periodic table). They have found $\alpha=0.7$ and $\alpha=0.4$, respectively, for TmES and Tm_2O_3. More information would be necessary to determine the correct values of these factors. In particular, the determination of the $V(\Gamma_\alpha,l,a)$ themselves would be of great interest. The relaxation-time measurements inside the ground quartet alone cannot give these values. Measurements of the Orbach process would have given complementary information. But, as we have seen in Sec. IV, for this purpose it would be necessary to go above 11°K, a temperature range where the relaxation time is too short to be accurately measured with our apparatus.

When one looks into details of the calculation of the angular variation, one sees that the Δ_{ad}^2 and Δ_{bd}^2 are almost constant in the angular range investigated and that the anisotropy comes from the anisotropy of the spectrum [via the $(E_d-E_a)/\hbar$ terms in Eq. (8)]. The small variation of the Δ_{ad}^2 and Δ_{bd}^2 is a consequence of the near equality of $A(\Gamma_{3g},\xi)$ and $A(\Gamma_{5g},0)$ which is not a specific property of the Γ_8 quartet.

VI. CONCLUSION

In this paper, we have shown that, by simple group theoretical considerations and without the necessity of finding normal modes of the clusters, it is possible to get the formal expression for the orbit-lattice Hamiltonian in the case of rare-earth ions. With this description, the calculation of the contribution of several shells of neighbors can easily be made. We have particularized the expression for O_h symmetry, but it is very easy to apply these results to any symmetry group. The method developed in the Appendix will permit the treatment of some problems where the determination of the cluster normal modes is too difficult. We have also shown that *all* the matrix elements of the orbit-lattice interaction can be related to usual tabulated matrix elements, thus, simplifying the calculations greatly.

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[32] J. Rosset, Ph.D. Thesis, Faculté des Sciences, Grenoble, 1968 (unpublished).

[33] R. G. Barnes, R. L. Mossbauer, E. Kankeleit, and J. M. Pointdexter, Phys. Rev. **136**, A175 (1964).

The special case of a Γ_8 quarter as a ground state was treated and compared to the experimental results of relaxation-time measurements. The two relaxation times predicted by the theory were clearly observed, and their ratio is nearly equal to the theoretical one. The observed angular variation is also very well explained. There is, however, a factor of 4 difference between theoretical and experimental values, and some complementary experiments on the MgO:Er^{3+} system will be necessary to explain this discrepancy.

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APPENDIX: CALCULATION OF $V(\Gamma_\alpha,l,a)$ PARAMETERS

The energy of an electron at a point $\mathbf{r}(r,\theta,\phi)$ due to charges q_i at $\mathbf{R}_i(R_i,\theta_i,\phi_i)$ is given by[34]

$$V(r,\theta,\varphi)=-\sum_i eq_i \sum_{l=0}^{\infty} \frac{r^l}{R_i^{l+1}} \sum_{m,t} \frac{4\pi}{2l+1} \times Z_{lm}{}^t(\theta_i,\varphi_i) Z_{lm}{}^t(\theta,\varphi)\,, \tag{A1}$$

where $Z_{lm}{}^t(\theta,\phi)$ are the tesseral harmonics defined as

$$\begin{aligned} t&=0: \quad Z_{l0}{}^0=Y_l{}^0\,,\\ t&=c: \quad Z_{lm}{}^c=(1/\sqrt{2})[Y_l{}^{-m}+(-)^m Y_l{}^m]\,,\\ t&=s: \quad Z_{lm}{}^s=(i/\sqrt{2})[Y_l{}^{-m}-(-)^m Y_l{}^m]\,. \end{aligned}$$

We write Eq. (A1) as

$$V(r,\theta,\varphi)=\sum_{l,m,t} r^l \gamma_{lm}{}^t Z_{lm}{}^t(\theta,\varphi)\,, \tag{A2}$$

with

$$\gamma_{lm}{}^t=-\sum_i \frac{4\pi e q_i}{2l+1}\,\frac{Z_{lm}{}^t(\theta_i,\varphi_i)}{R_i^{l+1}}\,.$$

Only the $\gamma_{lm}{}^t$ depend on the positions of the charges.

The parameters $V(\Gamma_\alpha,l,a)$ are defined, from Eqs. (4) and (A2), by

$$\sum_{l,a} V(\Gamma_\alpha,l,a)C(\Gamma_\alpha,l,a,\beta)=\left[\frac{\partial V}{\partial\sigma(\Gamma_\alpha,\beta)}\right]_{\text{eq}} =\sum_{l,m,t} r^l Z_{lm}{}^t(\theta,\varphi)\left[\frac{\partial\gamma_{lm}{}^t}{\partial\sigma(\Gamma_\alpha,\beta)}\right]_{\text{eq}}\,. \tag{A3}$$

As the $C(\Gamma_\alpha,l,a,\beta)$ are linear combinations of spherical harmonics, they can be expressed in terms of tesseral harmonics. The values of the $V(\Gamma_\alpha,l,a)$ are then found by equating the coefficients of the tesseral harmonics in Eq. (A3).

To calculate the derivatives $\partial\gamma_{lm}{}^t/\partial\sigma(\Gamma_\alpha,\beta)$, one writes the $\gamma_{lm}{}^t$ in terms of Cartesian coordinates of the position of the charge

$$\gamma_{lm}{}^t=A_{lm}{}^t\sum_i f_{lm}{}^t(X_i,Y_i,Z_i)=A_{lm}{}^t\sum_i f_i\,,$$

and one uses the formula

$$\frac{\partial\gamma_{lm}{}^t}{\partial\sigma(\Gamma_\alpha,\beta)}=A_{lm}{}^t\sum_{\substack{i\\u,v}}\frac{\partial f_i}{\partial X_i}\frac{\partial X_i}{\partial\sigma_{uv}}\frac{\partial\sigma_{uv}}{\partial\sigma(\Gamma_\alpha,\beta)} +\frac{\partial f_i}{\partial Y_i}\frac{\partial Y_i}{\partial\sigma_{uv}}\frac{\partial\sigma_{uv}}{\partial\sigma(\Gamma_\alpha,\beta)} +\frac{\partial f_i}{\partial Z_i}\frac{\partial Z_i}{\partial\sigma_{uv}}\frac{\partial\sigma_{uv}}{\partial\sigma(\Gamma_\alpha,\beta)}\,,$$

where the $\partial X_i/\partial\sigma_{uv}$ are obtained from the definition of σ_{uv} given in Eq. (1), and the $\partial\sigma_{uv}/\partial\sigma(\Gamma_\alpha,\beta)$ are easily deduced, for each symmetry group, from the definition of the $\sigma(\Gamma_\alpha,\beta)$ themselves. For the O_h group, the $\sigma(\Gamma_\alpha,\beta)$ are defined as[19]

$$\begin{aligned} \sigma(\Gamma_{1g})&=\epsilon(\Gamma_{1g})=(1/\sqrt{2})(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})\,,\\ \sigma(\Gamma_{3g},\xi)&=\epsilon(\Gamma_{3g},\xi)=(\sqrt{3}/2)(\epsilon_{xx}-\epsilon_{yy})\,,\\ \sigma(\Gamma_{3g},\theta)&=\epsilon(\Gamma_{3g},\theta)=\tfrac{1}{2}(2\epsilon_{zz}-\epsilon_{xx}-\epsilon_{yy})\,; \end{aligned}$$

$$\begin{aligned} \sigma(\Gamma_{4g},1)&=-(i/2)(\tfrac{3}{2})^{1/2}[\sigma_{yz}-\sigma_{zy}+i(\sigma_{zx}-\sigma_{xz})]\,,\\ \sigma(\Gamma_{4g},0)&=(i\sqrt{3}/2)(\sigma_{xy}-\sigma_{yx})\,,\\ \sigma(\Gamma_{4g},-1)&=(i/2)(\tfrac{3}{2})^{1/2}[\sigma_{yz}-\sigma_{zy}-i(\sigma_{zx}-\sigma_{xz})]\,; \end{aligned}$$

$$\begin{aligned} \sigma(\Gamma_{5g},1)&=\epsilon(\Gamma_{5g},1)=-i(\tfrac{3}{2})^{1/2}(\epsilon_{yz}+i\epsilon_{zx})\,,\\ \sigma(\Gamma_{5g},0)&=\epsilon(\Gamma_{5g},0)=i\sqrt{3}\epsilon_{xy}\,,\\ \sigma(\Gamma_{5g},-1)&=\epsilon(\Gamma_{5g},-1)=i(\tfrac{3}{2})^{1/2}(\epsilon_{yz}-i\epsilon_{zx})\,. \end{aligned}$$

As an illustration, we calculate $V(\Gamma_{3g},6)$ in the case of O_h group. From tables of Ref. 19, we find

$$C(\Gamma_{3g},6,\theta)=2(\pi/13)^{1/2}[(7^{1/2}/2\sqrt{2})Z_{60}{}^0+(1/2\sqrt{2})Z_{64}{}^c]\,.$$

From Eq. (A3), we obtain

$$V(\Gamma_{3g},6)\left(\frac{7\pi}{26}\right)^{1/2}=r^6\left[\frac{\partial\gamma_{60}{}^0}{\partial\sigma(\Gamma_{3g},\theta)}\right]_{\text{eq}}\,.$$

From Ref. 34, and with the same charge e' for all the neighboring ions of the same shell,

$$\gamma_{60}{}^0=-\frac{ee'}{8}\left(\frac{\pi}{13}\right)^{1/2} \times\sum_i \frac{231Z_i^6-315Z_i^4R_i^2+105Z_i^2R_i^4-5R_i^6}{R_i^{13}} =A_{60}{}^0\sum_i f_i\,.$$

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[34] M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 227.

We then calculate

$$\frac{\partial f_i}{\partial X_i}=\left[-\frac{(231)(13Z_i^6)}{R_i^{15}}+\frac{(315)(11Z_i^4)}{R_i^{13}}-\frac{(105)(9Z_i^2)}{R_i^{11}}+\frac{5X7}{R_i^9}\right]X_i=G_iX_i,$$

$$\frac{\partial f_i}{\partial Y_i}=G_iY_i,$$

$$\frac{\partial f_i}{\partial Z_i}=G_iZ_i+[(231)(6Z_i^4)-(315)(4Z_i^2R_i^2)+(105)(2R_i^4)]\frac{Z_i}{R_i^{13}}.$$

We have, in addition,

$$\frac{\partial\epsilon_{xx}}{\partial\epsilon(\Gamma_{3g},\theta)}=\frac{\partial\epsilon_{yy}}{\partial\epsilon(\Gamma_{3g},\theta)}=-\tfrac{1}{3},\quad\frac{\partial\epsilon_{zz}}{\partial\epsilon(\Gamma_{3g},\theta)}=\tfrac{2}{3},$$

$$\frac{\partial X_i}{\partial\epsilon_{xx}}=X_i^0,\quad\frac{\partial Y_i}{\partial\epsilon_{yy}}=Y_i^0,\quad\frac{\partial Z_i}{\partial\epsilon_{zz}}=Z_i^0,$$

so that

$$\frac{\partial\gamma_{60}{}^0}{\partial\epsilon(\Gamma_{3g},\theta)}=A_{60}{}^0\sum_i\tfrac{1}{3}\left\{(2Z_i^2-X_i^2-Y_i^2)G_i+\frac{2Z_i^2}{R_i^{13}}[(231)(6Z_i^4)-(315)(4Z_i^2R_i^2)+(105)(2R_i^4)]\right\}.$$

For sixfold coordination, one obtains easily

$$V(\Gamma_{3g},6)=7(7/2)^{1/2}(ee'\langle r^6\rangle/R^7).$$

For eightfold coordination,

$$V(\Gamma_{3g},6)=[(16)(14)^{1/2}/9](ee'\langle r^6\rangle/R^7).$$

For 12 equivalent neighbors (the second neighbors in CaF_2 and MgO structures, for instance),

$$V(\Gamma_{3g},6)=[(49)(14)^{1/2}/16](ee'\langle r^6\rangle/R^7).$$

The values of the $V(\Gamma_\alpha,l,a)$ for MgO structure ured in this paper are, taking into account nearest neighboss up to the fourth,

$$\begin{aligned}
V(\Gamma_{1g},4)&=5(14/3)^{1/2}(ee'\langle r^4\rangle/R^5)[1+(1/8\sqrt{2})-(8/81\sqrt{3})-(1/32)],\\
V(\Gamma_{1g},6)&=7(ee'\langle r^6\rangle/R^7)[1+(13/32\sqrt{2})+(64/729\sqrt{3})-(1/128)],\\
V(\Gamma_{3g},2)&=6(ee'\langle r^2\rangle/R^3)[1+(1/4\sqrt{2})-(8/27\sqrt{3})-(1/8)],\\
V(\Gamma_{3g},4)&=-5(5/3)^{1/2}(ee'\langle r^4\rangle/R^5)[1+(37/80\sqrt{2})+(32/405\sqrt{3})-(1/32)],\\
V(\Gamma_{3g},6)&=7(7/2)^{1/2}(ee'\langle r^6\rangle/R^7)[1-(7/64\sqrt{2})+(32/1701\sqrt{3})-(1/128)];\\
V(\Gamma_{4g},4)&=-2(35/3)^{1/2}(ee'\langle r^4\rangle/R^5)[1+(1/8\sqrt{2})-(8/81\sqrt{3})-(1/32)],\\
V(\Gamma_{4g},6)&=21^{1/2}(ee'\langle r^6\rangle/R^7)[1+(13/32\sqrt{2})+(64/729\sqrt{3})-(1/128)];\\
V(\Gamma_{5g},2)&=4(ee'\langle r^2\rangle/R^3)[1+(1/4\sqrt{2})-(8/27\sqrt{3})-(1/8)],\\
V(\Gamma_{5g},4)&=-2(5/3)^{1/2}(ee'\langle r^4\rangle/R^5)[1+(5/4\sqrt{2})+(40/81\sqrt{3})-(1/32)],\\
V(\Gamma_{5g},6,a)&=\tfrac{1}{2}(35/2)^{1/2}(ee'\langle r^6\rangle/R^7)[1+(13/32\sqrt{2})+(64/729\sqrt{3})-(1/128)],\\
V(\Gamma_{5g},6,b)&=\tfrac{3}{2}(77/2)^{1/2}(ee'\langle r^6\rangle/R^7)[1-(17/96\sqrt{2})+(64/6561\sqrt{3})-(1/128)];
\end{aligned}$$

where, in the brackets, the *i*th term is the contribution of the *i*th shell and e' is the effective charge of the oxygen ions.