Reduction of the Number of the Independent Orbit-Lattice Parameters

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It is shown that the long-wavelength approximation introduces some relations between the dynamic parameters which describe the orbit-lattice interaction. These relations, and also other relations which connect some of these parameters to the static parameters, are obtained from symmetry considerations. They reduce significantly the number of independent dynamic parameters, and this number is given for some common groups. The relations are derived explicitly for the O_h group.

I. INTRODUCTION

WITHIN the crystal-field model, a paramagnetic ion in substitution in a crystal is submitted to a potential V set up by the electric charges of the ligand ions. This potential satisfies the Laplace equation $\nabla^2 V=0$ and can then be expanded in terms of spherical harmonics or, appropriately using the symmetry properties of the system, in terms of linear combinations of the spherical harmonics which belong to the irreducible representations of the point group G of the ion site. Calling $Y(l,\Gamma_\alpha,a,\beta)$ the normalized combination of order l which belongs to the βth component of the irreducible representation Γ_α (the index a distinguishes between various sets of combinations associated with Γ_α) this expansion is

$$V=\sum_{l,\alpha,a,\beta} C(l,\Gamma_\alpha,a,\beta) r^l Y(l,\Gamma_\alpha,a,\beta), \quad (1)$$

where only the C coefficients depend on the environment. The static part of this potential, V_{st}, is clearly invariant and can be written as

$$V_{st}=\sum_{l,a} C(l,\Gamma_{1g},a)\,|_{eq} r^l Y(l,\Gamma_{1g},a) = \sum_{l,a} A(l,\Gamma_{1g},a) Y(l,\Gamma_{1g},a), \quad (2)$$

where Γ_{1g} is the trivial representation of G. The terms $A(l,\Gamma_{1g},a)$ are the usual static crystal-field "parameters" and they suffice to describe the static coupling between the ion and its environment.[1] There are N_S independent "parameters," N_S being determined from the symmetry group only. They can be calculated if new approximations are introduced such as, for example, the point-charge model for the ligand ions.

For the dynamic problem, one usually expands the potential (1) in terms of normal modes of the cluster consisting of the paramagnetic ion and its neighbors.[2,3] This expansion introduces "dynamic parameters." If only symmetry properties are used, there exists a definite number of independent parameters, this number depending on the number of neighbors introduced for the determination of the normal modes.

We have already shown[4] that the long-wavelength approximation enables us to fix the number of the parameters to a value N_v which depends on the symmetry only.

In this work, we shall show, using only the crystal-field model and the long-wavelength approximation, that the preceding dynamic parameters are in fact not independent but are related by some linear relations which depend on the symmetry only. We shall show also that some of them are related to the static parameters. These relations thus will reduce significantly the number of really independent dynamic parameters.

Before going into the details of the calculation, we point out that if, from the formal point of view, the long-wavelength approximation reduces the generality of the conclusions, it remains excellent for most of the phenomena resulting from the orbit-lattice coupling: relaxation via direct process and, most of the time, via Orbach process, static stress experiments, and ultrasonic experiments. In addition, for these relaxation processes, the phonon spectrum is well described by the Debye model, and the comparison between experimental results and theoretical calculations is then more significant.

In Sec. II, we show the existence of the relations between the dynamic parameters, and we give the outline of the method which permits us to get these relations in specific cases. In Sec. III, we derive the relations connecting static and dynamic parameters. Finally, in Sec. IV, we apply these results to the case of O_h symmetry.

II. RELATIONS BETWEEN DYNAMIC PARAMETERS

The long-wavelength approximation is equivalent to the assumption that the deformation of the lattice, responsible for the orbit-lattice coupling, is uniform in the vicinity of the paramagnetic ion, in a volume small compared to λ^3, λ being the wavelength of the active

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[1] K. W. H. Stevens, Proc. Phys. Soc. (London) **A65**, 209 (1952).

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

[3] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[4] M. Borg, R. Buisson, and C. Jacolin, Phys. Rev. B 1, 1917 (1970).

thermal waves. This deformation can then be described by the tensor σ_{uv} defined by

$$\sigma_{uv}=\frac{\partial \Delta r_u}{\partial r_v} \quad (u,v=x,y,z), \tag{3}$$

where r_u and Δr_u are, respectively, the coordinates of the point and the displacement components in this point.

Instead of expanding the potential (1) in terms of normal modes of a cluster, we expand it in terms of $\sigma(\Gamma_\alpha,b,\beta)$, the linear combinations of the Cartesian components σ_{uv} which belong to the irreducible representation of the symmetry group G (the index b distinguishes between several sets belonging to the same representation). This expansion gives the orbit-lattice interaction,[3] the first-order term of which is

$$V_{\mathrm{OL}}{}^{(1)}=\sum_{\substack{l,\alpha,a,\beta\\ \alpha',b,\beta'}}\left.\frac{\partial C(l,\Gamma_\alpha,a,\beta)}{\partial\sigma(\Gamma_{\alpha'},b,\beta')}\right|_{\mathrm{eq}} \times\sigma(\Gamma_{\alpha'},b,\beta')Y(l,\Gamma_\alpha,a,\beta). \tag{4}$$

The invariance of V_{OL} under the symmetry operations implies $\Gamma_{\alpha'}=\Gamma_\alpha{}^*$ and $\beta'=\beta$. To get a more explicit expression, we use the fact that the potential (1) set up at the point (r,θ,ϕ) by electric charges q_j at point (R_j,θ_j,ϕ_j) can be written, from the classical formula (see, for instance, Ref. 5) and using the orthogonality of the linear combinations of the spherical harmonics

$$V(r,\theta,\phi)=\sum_{l,j,\alpha,a,\beta}\frac{4\pi q_j}{2l+1}\frac{r^l}{R_j{}^{l+1}} \times Y^*(l,\Gamma_\alpha,a,\beta;\theta_j,\phi_j)Y(l,\Gamma_\alpha,a,\beta;\theta,\phi). \tag{5}$$

The charges q_j are not necessarily localized charges. Equation (5) remains true if the electric charge of the ligand ions is distributed around their nucleus. (We have supposed that there is no "overlap" between the ligands and paramagnetic ion charge distributions; see the conclusion.) In that case, the sum $\sum_j$ must be replaced by an integral over the region occupied by the electrons of the ligand, q_j being the charge contained in a small volume $d\tau$ surrounding the point (R_j,θ_j,ϕ_j) or, more precisely, the density probability for the electrons: $\psi^*(R_j,\theta_j,\phi_j)\psi(R_j,\theta_j,\phi_j)d\tau$.

The important point to be noted is that these elementary charges in equilibrium positions can be grouped in "shells" which are invariant under the operations of the point group. As the contributions of the various "shells" to the potential are additive and independent, we shall suppose from this point on that there is only one "shell." The sum $\sum_j$ is then replaced by $\sum_{js}$, a sum over the charges of the shell s. The orbit-lattice potential originated by the shell s can then be written as

$$\begin{aligned}V_{\mathrm{OL}(s)}{}^{(1)}=&\sum_{l,js}\frac{4\pi q_{js}}{2l+1}r^l\sum_{\alpha,a,b,\beta}\left\{\frac{\partial}{\partial\sigma(\Gamma_\alpha{}^*,b,\beta)}\right.\\ &\left.\times\left[\frac{1}{R_{js}{}^{l+1}}Y^*(l,\Gamma_\alpha,a,\beta;\theta_{js},\phi_{js})\right]\right\}_{\mathrm{eq}}\\ &\times Y(l,\Gamma_\alpha,a,\beta;\theta,\phi)\sigma(\Gamma_\alpha{}^*,b,\beta)\\ =&\sum_{l,\alpha,a,b,\beta}V_s(l,\Gamma_\alpha,a,b)\\ &\times Y(l,\Gamma_\alpha,a,\beta;\theta,\phi)\sigma(\Gamma_\alpha{}^*,b,\beta),\end{aligned} \tag{6}$$

where

$$V_s(l,\Gamma_\alpha,a,b)=\sum_{js}\frac{4\pi q_{js}}{2l+1}r^l\left\{\frac{\partial}{\partial\sigma(\Gamma_\alpha{}^*,b,\beta)} \times\left[\frac{1}{R_{js}{}^{l+1}}Y^*(l,\Gamma_\alpha,a,\beta;\theta_{js},\phi_{js})\right]\right\}_{\mathrm{eq}}. \tag{7}$$

As the $\sum_{js}$ in (7) is over all the "equivalent" (under the symmetry operations) charges, $V_s(l,\Gamma_\alpha,a,b)$ is invariant and belongs to the Γ_{1g} representation. It is easy to see that only the invariant part of *each* term of the sum contributes to the result, the noninvariant parts being cancelled on the summation. It is then convenient to use the Dirac notation and, as the differential operator $\partial/\partial\sigma(\Gamma_\alpha{}^*,b,\beta)$ belongs to the representation Γ_α, to denote

$$O(\Gamma_\alpha,b,\beta)=\frac{\partial}{\partial\sigma(\Gamma_\alpha{}^*,b,\beta)}.$$

We can then rewrite (7) as

$$V_s(l,\Gamma_\alpha,a,b)=\frac{4\pi q_{js}}{2l+1}r^l n_s\sum_{l',a'}\left\langle Y(l',\Gamma_{1g},a')\middle|O(\Gamma_\alpha,b,\beta)\right. \times\left|\frac{1}{R^{l+1}}Y^*(l,\Gamma_\alpha,a,\beta)\right\rangle_{R=R_{js0}}Y(l',\Gamma_{1g},a';\theta_{js0},\phi_{js0}), \tag{8}$$

where n_s is the number of charges of the shell s, and $(R_{js0},\theta_{js0},\phi_{js0})$ are the equilibrium coordinates of any one of the charges of the shell. To obtain this expression, we have projected each term of (7) on the invariants $Y(l',\Gamma_{1g},a')$.

We shall now show that it is possible to transform each term of the sum (8) into a product of two terms, one of which depends on the symmetry only.

We first calculate the matrix element

$$\left\langle Y_{l'}{}^{m'}\middle|\frac{\partial}{\partial\sigma_{uv}}\middle|\frac{1}{R^{l+1}}Y_l{}^m\right\rangle. \tag{9}$$

From the definition (3) we have

$$\frac{\partial}{\partial\sigma_{vu}}=O_{vu}=\frac{\partial R_v}{\partial\sigma_{vu}}\frac{\partial}{\partial R_v}=R_u\frac{\partial}{\partial R_v}=R_u\nabla_v. \tag{10}$$

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

As the Y_l^m form a complete set, we have

$$\left\langle Y_{l'}^{m'}\left|O_{vu}\right|\frac{1}{R^{l+1}}Y_l^m\right\rangle=\sum_{l'',m''}\langle Y_{l'}^{m'}|R_u|Y_{l''}^{m''}\rangle \times\left\langle Y_{l''}^{m''}\left|\nabla_v\right|\frac{1}{R^{l+1}}Y_l^m\right\rangle.$$

If **a** is a polar vector we can write, from the Wigner-Eckart theorem,

$$\langle Y_{l'}^{m'}|R_u|Y_{l''}^{m''}\rangle=\Re(l',l'')\langle l',m'|a_u|l'',m''\rangle,$$

$$\left\langle Y_{l''}^{m''}\left|\nabla_v\right|\frac{Y_l^m}{R^{l+1}}\right\rangle=\mathfrak{N}(l'',l)\langle l'',m''|a_v|l,m\rangle,$$

the constants $\Re(l',l'')$ and $\mathfrak{N}(l'',l)$ being different from zero only for $l'=l''\pm1$ and $l''=l\pm1$. The well-known quantities

$$\begin{aligned}\langle l-1,\,m\pm1|a_\pm|l,m\rangle&=\langle l,m|a_\mp|l-1,\,m\pm1\rangle\\&=\pm[(l\mp m)(l-1\mp m)]^{1/2},\\\langle l-1,\,m|a_z|l,m\rangle&=\langle l,m|a_z|l-1,\,m\rangle\\&=(l^2-m^2)^{1/2},\end{aligned}\tag{11}$$

where $a_\pm=a_x\pm ia_y$, are improperly so written because they are not the matrix elements of the components of the vector **a**; they are only proportional to them. The notation used here supposes the multiplicative factor, which depends on l, is included in the constants $\Re$ and $\mathfrak{N}$.

One can show that $\mathfrak{N}(l-1,\,l)=0$. In effect the relation

$$\left\langle Y_{l-1}^{m}\left|\left|\frac{\partial}{\partial z}\right|\frac{1}{R^{l+1}}Y_l^m\right\rangle=\mathfrak{N}(l-1,l)(l^2-m^2)^{1/2}$$

becomes, for $m=0$,

$$\left\langle Y_{l-1}^{0}\left|\frac{\partial}{\partial z}\right|\frac{1}{R^{l+1}}Y_l^0\right\rangle=l\mathfrak{N}(l-1,l),$$

and, from the formula[6] for the gradient or from the derivatives of the spherical harmonics given, for instance, by Stevens,[7] one finds

$$l\mathfrak{N}(l-1,l)=\frac{1}{r^{l+2}}\times\left[l\left(\frac{2l+1}{2l-1}\right)^{1/2}-(2l+1)(\tfrac{4}{3}\pi)^{1/2}\langle Y_{l-1}^{0}|Y_1^0|Y_l^0\rangle\right]=0.$$

The matrix element (9) can then be written

$$\left\langle Y_{l'}^{m'}\left|O_{vu}\right|\frac{1}{R^{l+1}}Y_l^m\right\rangle=\sum_{l'',m''}K(l',l'',l)\times\langle l',m'|a_u|l'',m''\rangle\langle l'',m''|a_v|l,m\rangle,\tag{12}$$

where $K(l',l'',l)=\Re(l',l'')\mathfrak{N}(l'',l)$.

[6] M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., *The 3-j and 6-j symbols* (Technology Press, Cambridge, Mass., 1959).

[7] K. W. H. Stevens, Rept. Progr. Phys. **30**, 189 (1967).

The only nonzero constants for our problem are $K(2,3,2)$, $K(4,3,2)$, $K(4,5,4)$, $K(6,5,4)$, $K(6,7,6)$, $K(8,7,6)$. Their explicit forms can easily be found but they are not necessary for the present analysis.

We can then transform (8) because the matrix elements appearing in it are linear combinations of the matrix elements (9) or (12). To do this transformation, we use the relation

$$O(\Gamma_\alpha,b,\beta)=\sum_{u,v}\lambda_{uv}(\Gamma_\alpha,b,\beta)O_{uv},$$

where the $\lambda_{uv}(\Gamma_\alpha,b,\beta)$ are specific for a group and are defined by

$$T(\Gamma_\alpha,b,\beta)=\sum_{u,v}\lambda_{uv}(\Gamma_\alpha,b,\beta)a_ua_v,$$

$T(\Gamma_\alpha,b,\beta)$ being the components of the tensor obtained from tensorial product of a polar vector **a** by itself. Then, Eq. (8) becomes

$$\begin{aligned}V_s(l,\Gamma_\alpha,a,b)=&\frac{4\pi q_{js}}{2l+1}r^l n_s\\&\times\{\sum_{a'}K(l,\,l+1,\,l)Y(l,\Gamma_{1g},a';\,\theta_{js0},\phi_{js0})\\&\times[\sum_{u,v,m''}\lambda_{uv}(\Gamma_\alpha,b,\beta)\langle Y(l,\Gamma_{1g},a')|a_v|l+1,\,m''\rangle\\&\times\langle l+1,\,m''|a_u|Y(l,\Gamma_\alpha,a,\beta)\rangle]+\sum_{a''}K(l+2,\,l+1,\,l)\\&\times Y(l+2,\,\Gamma_{1g},\,a'';\,\theta_{js0},\,\phi_{js0})[\sum_{u,v,m''}\lambda_{uv}(\Gamma_\alpha,b,\beta)\\&\times\langle Y(l+2,\,\Gamma_{1g};\,a'')|a_v|l+1,\,m''\rangle\\&\times\langle l+1,\,m''|a_u|Y(l,\Gamma_\alpha,a,\beta)\rangle]\}.\end{aligned}\tag{13}$$

The expressions inside the brackets appearing in Eq. (13) depend only on the symmetry and can easily be evaluated for any group. The multiplicative factors associated with these expressions depend on the particular shell considered but they are independent of the representation Γ_α and of the indexes a and b. It is then possible, for a fixed value of l, to eliminate these multiplicative factors between the various equations obtainable from Eq. (13) for various values of the indexes α, a, b. This elimination gives linear relations between the parameters $V_s(l,\Gamma_\alpha,a,b)$ associated with fixed value of l, and these relations depend on the symmetry only. The true dynamic parameters, being obtained from a sum of the values of $V_s(l,\Gamma_\alpha,a,b)$ over the shells, are related by the same relations.

The number N_v of the parameters $V(l,\Gamma_\alpha,a,b)$ can be determined from the reduction of the $\mathfrak{D}_l$ representation in terms of the irreducible representations of g. Let

TABLE I. Number of the various parameters defined in the text for some common point groups.

Point group	N_S				N_v				N_I'				N_I			
	$l=2$	$l=4$	$l=6$	Total	$l=2$	$l=4$	$l=6$	Total	$l=2$	$l=4$	$l=6$	Total	$l=2$	$l=4$	$l=6$	Total
O_h	0	1	1	2	2	4	5	11	1	2	2	5	1	1	1	3
D_{3h}	1	1	2	4	5	6	11	22	2	3	4	9	1	2	2	5
C_{3h}	1	1	3	5	9	11	21	41	2	4	6	12	1	3	3	7
C_{3v}	1	2	3	6	8	14	20	42	3	5	6	14	2	3	3	8
C_{4v}	1	2	2	5	6	11	15	32	3	4	5	12	2	2	3	7

this reduction be

$$\mathfrak{D}_l=\sum_\alpha n_{l\alpha}\Gamma_\alpha.$$

Equation (6) shows that the number of the parameters $V(l,\Gamma_\alpha,a,b)$ is, for fixed l and α, equal to the number of couples (a,b). a can take $n_{l\alpha}$ values, while b can take $(n_{0\alpha}+n_{1\alpha}+n_{2\alpha})$ because the components of the tensor σ_{uv} belong to the sum $(\mathfrak{D}_0+\mathfrak{D}_1+\mathfrak{D}_2)$. The number of couples (a,b) is then $n_{l\alpha}(n_{0\alpha}+n_{1\alpha}+n_{2\alpha})$. For the same reasons as in the static case, l can take only the values $l=2$, 4 for iron-group ions, and $l=2$, 4, 6 for rare-earth ions. Thus, for the last case we have

$$N_v=\sum_{\alpha,l=2,4,6} n_{l\alpha}(n_{0\alpha}+n_{1\alpha}+n_{2\alpha}).$$

The number of the multiplicative factors considered above is equal, for each value of l, to the number of the linear combinations of the spherical harmonics of order l and $l+2$ belonging to the trivial representation Γ_{1g}. The total number of these factors is then

$$N_I'=\sum_{l=2,4,6}(n_{l,1g}+n_{l+2,1g}).$$

N_I' is also the number of the independent parameters and (N_V-N_I') is the number of the relations obtained with the method indicated. Table I gives the values of N_v and N_I' for some common point groups.

To obtain the relations between the dynamic parameters for a given group, it is useful to introduce the operators $O(\mathfrak{D}_\alpha,\beta)$, with $\mathfrak{D}_\alpha=\mathfrak{D}_{0g}$, $\mathfrak{D}_{1g}$, $\mathfrak{D}_{2g}$, which are the linear combinations of the operators O_{uv} belonging to the representation $\mathfrak{D}_\alpha$ of the rotation-inversion group. The operators are given by

$$O(\mathfrak{D}_{0g})=(1/\sqrt{3})[R_z\nabla_z+\tfrac{1}{2}(R_+\nabla_-+R_-\nabla_+)];$$
$$O(\mathfrak{D}_{1g},0)=(1/2\sqrt{2})(R_-\nabla_+-R_+\nabla_-),$$
$$O(\mathfrak{D}_{1g},\pm1)=\tfrac{1}{2}(R_\pm\nabla_z-R_z\nabla_\pm);$$
$$O(\mathfrak{D}_{2g},0)=(1/\sqrt{6})[2R_z\nabla_z-\tfrac{1}{2}(R_+\nabla_-+R_-\nabla_+)],$$
$$O(\mathfrak{D}_{2g},\pm1)=\tfrac{1}{2}(R_\pm\nabla_z+R_z\nabla_\pm),$$
$$O(\mathfrak{D}_{2g},\pm2)=\tfrac{1}{2}R_\pm\nabla_\pm;$$

and their matrix elements are easily obtained using Eqs. (11) and (12). Before going to the calculation for the O_h group, we now show that some of the N_I' dynamic parameters are related to static parameters.

III. RELATIONS BETWEEN STATIC AND DYNAMIC PARAMETERS

There exist relations between static and dynamic parameters because the differential operators associated with the trivial representation act like a constant

$$O(\Gamma_{1g},b)=\frac{\partial}{\partial\sigma(\Gamma_{1g},b)}=\mu(b). \tag{14}$$

In particular, the operator associated with the trivial representation arising from the representation $\mathfrak{D}_{0g}$ is simply $(1/\sqrt{3})(\mathbf{R}\cdot\mathbf{grad})$ and the corresponding constant $\mu(b)$ is $-(l+1)/\sqrt{3}$.

Equation (8) is simplified when one uses the form of $O(\Gamma_{1g},b)$ given by Eq. (14). We then obtain

$$V_s(l,\Gamma_{1g},a,b)=\frac{4\pi q_{js}}{2l+1}r^l n_s\mu(b)\frac{1}{R_{js0}{}^{l+1}}Y(l,\Gamma_{1g},a;\theta_{js0},\phi_{js0}).$$

On the other hand, the static parameters $A(l,\Gamma_{1g},a)$ defined in Eq. (2) can easily be calculated from Eq. (5). The contribution of the shell s is[8]

$$A_s(l,\Gamma_{1g},a)=\frac{4\pi q_{js}}{2l+1}r^l n_s\frac{1}{R_{js0}{}^{l+1}}Y(l,\Gamma_{1g},a;\theta_{js0},\phi_{js0}). \tag{15}$$

The comparison between the two last equations gives the relations

$$V(l,\Gamma_{1g},a,b)=\mu(b)A(l,\Gamma_{1g},a).$$

The number of these relations is equal to the number of the static parameters $N_S=\sum_l n_{l,1g}$.

Finally, the number of new parameters necessary to describe the dynamic problems is $N_I=N_{I'}-N_S$. The table gives the value of N_I for some symmetry groups.

These relations cannot be strictly compared to the relations proposed by Orbach[3] because the latter were phenomenological and they related *all* the dynamic parameters to the static parameters. The numerical factor $\mu(b)$ can be important (see Sec. IV) as was pointed out by Huang.[9]

[8] This formula simplifies the calculation for the parameters $A(l,\Gamma_{1g},a)$ if a particular approximation, like the point-charge model, is used.

[9] C.-Y. Huang, Phys. Rev. **139**, A241 (1965).

IV. APPLICATION TO O_h GROUP

For the particular case of the O_h group, there are $N_v=11$ parameters, as the table shows. The two parameters associated to $l=2$ are proportional because $K(2,3,2)=0$. We then have

$$V_s(2,\Gamma_{3g})=\tfrac{4}{5}\pi q_{js}r^2 n_s K(4,3,2)Y(4,\Gamma_{1g},\theta_{js0},\phi_{js0}) \times\sum_{u,v,m''}\lambda_{uv}(\Gamma_{3g},\theta)\langle Y(4,\Gamma_{1g})\,|\,a_v\,|\,Y_3{}^{m''}\rangle \times\langle Y_3{}^{m''}\,|\,a_u\,|\,Y(2,\Gamma_{3g},\theta)\rangle,$$

$$V_s(2,\Gamma_{5g})=\tfrac{4}{5}\pi q_{js}r^2 n_s K(4,3,2)Y(4,\Gamma_{1g},\theta_{js0},\phi_{js0}) \times\sum_{u,v,m''}\lambda_{uv}(\Gamma_{5g},0)\langle Y(4,\Gamma_{1g})\,|\,a_v\,|\,Y_3{}^{m''}\rangle \times\langle Y_3{}^{m''}\,|\,a_u\,|\,Y(2,\Gamma_{5g},0)\rangle.$$

From the explicit form of the $Y(l,\Gamma_\alpha,\beta)$ and of the $\lambda_{uv}(\Gamma_\alpha,\beta)$ which can be found, for instance, in the tables of Griffith[10] we find

$$V(2,\Gamma_{3g})/V(2,\Gamma_{5g})=\tfrac{3}{2}.$$

For the parameters associated to $l=4$, one can find two relations. Denoting

$$I_4=\sum_s(4\pi q_{js}r^4/9)n_s K(4,5,4)Y(4,\Gamma_{1g};\theta_{js0},\phi_{js0}),$$

$$I_4'=\sum_s(4\pi q_{js}d^0/9)n_s K(6,5,4)Y(6,\Gamma_{1g};\theta_{js0},\phi_{js0}),$$

we find

$$V(4,\Gamma_{1g})=(55/\sqrt{3})I_4,$$
$$V(4,\Gamma_{3g})=-4(35/6)^{1/2}I_4-9(\sqrt{5})I_4',$$
$$V(4,\Gamma_{4g})=-11(10/3)^{1/2}I_4,$$
$$V(4,\Gamma_{5g})=(70/3)^{1/2}I_4-12(\sqrt{5})I_4'.$$

Eliminating I_4 and I_4', we obtain

$$V(4,\Gamma_{1g})=-(\tfrac{5}{2})^{1/2}V(4,\Gamma_{4g}),$$
$$3V(4,\Gamma_{5g})+(7)^{1/2}V(4,\Gamma_{4g})=4V(4,\Gamma_{3g}).$$

For the parameters with $l=6$, we need an invariant form of the spherical harmonics with $l=8$. This form is

$$Y(8,\Gamma_{1g})=(33/64)^{1/2}Y_8{}^0+(7/96)^{1/2}(Y_8{}^4+Y_8{}^{-4}) +(65/384)^{1/2}(Y_8{}^8+Y_8{}^{-8}).$$

Denoting

$$I_6=\sum_s(4\pi q_{js}r^6/13)n_s K(6,7,6)Y(6,\Gamma_{1g};\theta_{js0},\phi_{js0}),$$

$$I_6'=\sum_s(4\pi q_{js}r^6/13)n_s K(8,7,6)Y(6,\Gamma_{1g};\theta_{js0},\phi_{js0}),$$

we obtain

$$V(6,\Gamma_{1g})=35\sqrt{3}I_6,$$
$$V(6,\Gamma_{3g})=(\sqrt{42})I_6+6(\sqrt{77})I_6',$$
$$V(6,\Gamma_{4g})=15(\sqrt{7})I_6,$$
$$V(6,\Gamma_{5g},a)=\tfrac{5}{2}(105/2)^{1/2}I_6,$$
$$V(6,\Gamma_{5g},b)=-\tfrac{1}{2}(231/2)^{1/2}I_6+16(\sqrt{7})I_6',$$

and also the relations

$$V(6,\Gamma_{1g})=(7/3)^{1/2}V(6,\Gamma_{4g})=3(14/5)^{1/2}V(6,\Gamma_{5g},a),$$
$$(13/\sqrt{5})V(6,\Gamma_{5g},a)+3(\sqrt{11})V(6,\Gamma_{5g},b)=8V(6,\Gamma_{3g}).$$

The relations between static and dynamic parameters for the O_h group are

$$V(4,\Gamma_{1g})=-(5/\sqrt{3})A(4,\Gamma_{1g}),$$
$$V(6,\Gamma_{1g})=-(7/\sqrt{3})A(6,\Gamma_{1g}).$$

As the table shows, only three new "parameters" are necessary to describe the first-order dynamic coupling. We have calculated in Ref. 4 the parameters $V(l,\Gamma_\alpha,a,b)$ for O_h symmetry with the point-charge approximation and up to the fourth neighbors. It is easy to see that the results verify all the above relations.

V. COMMENTS AND CONCLUSION

For the calculation of the relaxation times, as well as for the evaluation of static stresses, qualitative considerations were generally used to estimate the various dynamic parameters[3,9] or use was made of particular models, such as the point-charge model, to calculate them. The comparison between the calculated value and the experimental results was then unable to show where the origin of the disagreement is. This work, reducing notably the number of the independent parameters, permits one to write the relaxation times as functions of these parameters; and, when the experimental informations are sufficient, it will be possible to deduce the value of the parameters from the results, as for the static case. The comparison with the calculated values will then be more significant.

This reduction of the number of the independent dynamic parameters has a more fundamental meaning than the inherent reduction in using the point-charge model for the ligand ions. With this model, the mean value of the radial distance of the magnetic electrons $\langle r^n\rangle$ and the distance from the central ion to the ligands R_s appears as parameters. But it is clear that the number of the R_s (which must be considered as independent because the translational symmetry can be perturbed around the magnetic ion) depend on the number of ligands used for the calculation. We point out that, on the contrary, the relations connecting the dynamic parameters were obtained using only the point-group symmetry. They then remain valid even with a dis-

[10] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge U. P., New York, 1961).

tortion of the lattice by the magnetic ion if this distortion leaves the symmetry unchanged.

We also note that these relations are also correct in the "overlap" approximation for the covalency, because as long as only Coulombian energy is considered, the Laplace equation becomes then $\nabla^2 V = 4\pi\rho$, ρ being the spherical charge density, and only the radial part of the expansion (1) is modified.[11] Obviously, if exchange forces are included, our description is not valid.

[11] This point was called to our attention by Dr. D. K. Ray.

In addition to the reduction of the number of parameters, this work establishes formulas [(13) and (15)] which, once the standard combinations $Y(l,\Gamma_\alpha,a,\beta)$ and $T(\Gamma_\alpha,b,\beta)$ are known, gives, for any environment, the values of the parameters with a minimum amount of calculation.

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Angle Dependence of Paramagnetic-Resonance Line Intensities of Trivalent Cr^{53} in MgO†

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Three methods have been used to predict paramagnetic-resonance line intensities in the spectrum of trivalent Cr^{53} in sites of tetragonal symmetry in MgO. The methods are: numerical diagonalization of the Hamiltonian matrix, perturbation theory, and a technique involving the magnetic field induced at the nucleus by the electron spin. Experimentally observed line intensities are compared with the calculated intensities. The induced-field method is found to adequately describe the spectrum and to agree very closely with results from numerical diagonalization of the Hamiltonian. Some small discrepancies in line positions are observed which imply an inaccuracy in the usual axial-field spin Hamiltonian.

I. INTRODUCTION

THE angular dependence of transition probabilities in electron paramagnetic resonance (EPR) becomes complicated when the applied magnetic field and crystalline electric field compete as a quantization axis in the presence of a hyperfine interaction. Additional transitions are observable because the states may be mixed by matrix elements of the hyperfine interaction and crystal field operators. The magnetic dipole selection rule ($\Delta M = \pm 1$) is valid if applied to the base states $|M_S,M_I\rangle = |M,m\rangle$, but breaks down completely at some orientations if applied to the mixed states. This results in the appearance of so-called forbidden hyperfine lines in the EPR spectrum. For the case of small crystalline field splittings, adequate explanations of the existence of these forbidden transitions using perturbation techniques have been given by previous authors,[1,2] particularly for the ions of manganese and vanadium.

For the cases where the crystalline field splitting is comparable to or larger than the Zeeman splitting, the angle-dependent spectrum is very complicated and only direct diagonalization of the full Hamiltonian is adequate. For the intermediate cases Bir[3] and Bir and Sochava[4] have developed a technique which we call the induced-field method, which relies on the calculation of the magnetic field induced at the nucleus by the electron spin. In the induced-field method, either perturbation theory or diagonalization techniques may be employed but in either case only on the electronic portion of the Hamiltonian. The present work was done at X-band frequencies, for which the Zeeman splitting is about twice that of the crystal field. It successfully uses the induced-field method to explain the angular dependence of the Cr^{53} spectra in the tetragonal sites of magnesium oxide. It is the first report of chromium-forbidden hyperfine transitions.

The EPR spectrum of trivalent chromium is readily observed in ionic crystals and has been extensively studied, particularly as a dilute impurity in aluminum oxide[5,6] and magnesium oxide.[7,8] The latter crystal is

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