SOVIET PHYSICS JETP VOLUME 16, NUMBER 5 MAY, 1963

SYMMETRY THEORY FOR SPIN-PHONON INTERACTION

A. K. MOROCHA

Physico-technical Institute, Kazan' branch, Academy of Sciences, U.S.S.R.

Submitted to JETP editor May 25, 1962

J. Exptl. Theoret. Phys. (U.S.S.R.) **43**, 1804-1812 (November, 1962)

Group theory methods are used to derive a Hamiltonian for spin-phonon interaction in crystals with several constants which include all the possible mechanisms for spin-phonon interaction. It is proposed that these constants be found from experiment.

It is well known (cf., for example,[1]) that the spin Hamiltonian method is very fruitful for the description of paramagnetic resonance spectra in crystals. This method enables one to characterize the paramagnetic resonance spectrum by a few constants, whose determination is the central problem of experiments in the field of paramagnetic resonance. The problem for theory is to obtain these constants from some definite model for the crystal. One may ask: Can one describe the spin-phonon interaction by introducing a definite number of parameters which depend on the nature of the mechanism of spin-phonon interaction? In the present paper, using group theory methods, we shall show how one can obtain the Hamiltonian for the spin-phonon interaction by using the symmetry properties of the vibrations of the particles surrounding the paramagnetic ion and the symmetry properties of the wave functions of the paramagnetic ion, which are assumed to be known (for example, from the spin Hamiltonian).

1. GENERAL RELATIONS

Let us consider the two-particle function for the interaction between particles in a crystal containing paramagnetic ions:

$$V = \sum_{i>k} V_{ik} (\mathbf{r}_{ik}; \mathbf{S}_i \mathbf{S}_k), \tag{1}$$

where $|\mathbf{r}_{ik}| = \sqrt{(x_i - x_k)^2 + (y_i - y_k)^2 + (z_i - z_k)^2}$ is the distance between the particles at the i-th and j-th sites in the crystal lattice, $\mathbf{S}_i$ and $\mathbf{S}_k$ are the corresponding spin variables. Of all the interactions in (1), we shall be interested only in those interactions of the paramagnetic particles with one another and with other (nonmagnetic) particles which depend on the values of the magnetic moments. Under the influence of the lattice vibrations, these interactions will vary. This variable part of the coupling energy (1) gives the operator $\mathcal{H}_{sp}$ for the spin-phonon interaction. Usually one assumes some relaxation mechanism, finds the explicit form of the operator $\mathcal{H}_{sp}$,[2,3] and then the problem reduces to finding the matrix elements of $\mathcal{H}_{sp}$ between the energy levels given by the spin Hamiltonian. Without considering any specific interaction mechanism, we want to start from the symmetry properties and get expressions for the matrix elements in terms of several independent parameters which take account of all the possible mechanisms for spin-phonon interaction.

We start from the fact that every interaction of the paramagnetic particle with the lattice must be invariant with respect to the symmetry group G for its location in the lattice. Here we are obviously making the same approximation as in the theory of small vibrations, assuming that the symmetry of the displaced configuration of the particles differs negligibly from the symmetry of the equilibrium configuration. If in addition we make the natural assumption that the main contribution to this interaction comes only from binding to nearest neighbors, the symmetry of $\mathcal{H}_{sp}$ is determined by the symmetry of the position of the nearest particles surrounding the particular paramagnetic particle (or ion). Now, by introducing the symmetry coordinates $Q^{\alpha}_{j,k}$ for these nearest neighbors and using (1), we can write the general expression for $\mathcal{H}_{sp}$ in the following invariant form:

$$\mathcal{H}_{\mathrm{sp}} = \frac{1}{2} \sum_{k} \Big(\sum_{\alpha, j} V^{\alpha}_{j,k} Q^{\alpha}_{j,k} + \sum_{\alpha, \beta, i, j} W^{\alpha\beta}_{ij,k} Q^{\alpha}_{i,k} Q^{\beta}_{j,k} \Big). \tag{2}$$

Here $V^{\alpha}_{j,k} = \partial V_k / \partial Q^{\alpha}_{j,k}$ and $W^{\alpha\beta}_{ij,k} = \partial^2 V_k / \partial Q^{\alpha}_{i,k} \partial Q^{\beta}_{j,k}$ are functions depending only on the coordinates of the k-th paramagnetic particle and the particles immediately surrounding it; α labels the irreducible representation of the group G; j labels the corresponding term in the α-th irreducible representation.

The symmetry coordinates $Q^{\alpha}_{j,k}$ are linear combinations of the relative displacements u_{ik}^{σ} of the nearest particles:

$$Q_{j,k}^{\alpha} = \sum_{i\sigma} B_{ij,\sigma}^{\alpha} u_{ik}^{\sigma} \qquad (\sigma = x, y, z), \tag{3}$$

which in turn can be expressed in terms of quantities characterizing the lattice:[4]

$$u_{ik}^{\sigma} = \left(\frac{2\hbar}{M}\right)^{1/2} \sum_{p} \omega_p^{-1/2} \Phi_{p\sigma} (a_p^{+} + a_p) \cos (\mathbf{k}_p \mathbf{r}_{ik} + \Delta_p), \tag{4}$$

where M is the mass of the crystal, $\Phi_{p\sigma}$ is the unit polarization vector for the p-th normal lattice vibration; a_p^{+} and a_p are the creation and annihilation operators for phonons with frequency ω_p and wave vector $\mathbf{k}_p$; Δ_p is an arbitrary phase.

We introduce the notation

$$A_{j,p}^{\alpha,k} = \left(\frac{2\hbar\omega_p}{Mv^2}\right)^{1/2} \sum_{i\sigma} B_{ij,\sigma}^{\alpha} \Phi_{p\sigma} \cos (\mathbf{k}_p \mathbf{r}_{ik} + \Delta_p), \qquad P_p = a_p^{+} + a_p$$

and rewrite (2) in the form

$$\mathcal{H}_{\text{sp}} = \frac{1}{2} \sum \Bigg(\sum_{\alpha, j, p} V_{j,k}^{\alpha} A_{j,p}^{\alpha,k} P_p + \sum_{\alpha, \beta, i, j, p, q} W_{ij,k}^{\alpha\beta} A_{i,p}^{\alpha,k} A_{j,q}^{\beta,k} P_p P_q + \ldots \Bigg). \tag{5}$$

From now on we shall assume that all the paramagnetic particles are identical. Then if we neglect the effect of particles located on the boundary of the crystal, the summation over k in (5) reduces to multiplication by the total number N of paramagnetic particles. Expression (5) is convenient in that it enables us, on the basis of Koster's theorem[5] to write the matrix elements of $\mathcal{H}_{\text{sp}}$ between wave functions which transform irreducibly under the symmetry operations of the group G.

In the absence of the magnetic field, the energy levels of the paramagnetic particle will have the degeneracy allowed by the symmetry of the crystal. The degenerate wave functions belonging to a given energy level may be chosen to be a basis of an irreducible representation of the group G. Also, we shall be interested in a system of degenerate levels which are close to one another ($\sim 1 \text{ cm}^{-1}$) but far from other levels of the paramagnetic particle in the crystalline field. Thus, when the magnetic field becomes large, it is sufficient to treat the interaction only between close-lying levels.

Suppose we have an energy level E_α, belonging to the irreducible representation $\Gamma_\alpha \in G$ with eigenfunctions Ψ_i^{α} ($i = 1, \ldots, n_\alpha$, where n_α is the degree of degeneracy), and a close-lying level E_β with eigenfunctions Ψ_j^{β} ($j = 1, \ldots, m_\beta$), $E_\beta - E_\alpha = \Delta$. Following Koster,[16] we can immediately write the matrix of $\mathcal{H}_{\text{sp}}$ between the states E_α and E_β (and within them):

$$\begin{aligned} \mathcal{H}_{\text{sp}}^{\alpha\beta}(m \to n) &= \frac{1}{2} \sum_{k,p} P_p \langle \Psi_m^{\alpha} \Big| \sum_{\gamma} \sum_{j=1}^{n_\gamma} V_{j,k}^{\gamma} A_{j,p}^{\gamma,k} \Big| \Psi_n^{\beta} \rangle + \ldots \\ &= \frac{1}{2} \sum_{k,p,\gamma} \sum_{j=1}^{n_\gamma} A_{j,p}^{\gamma,k} P_p \langle \Psi_m^{\alpha} | V_{j,k}^{\gamma} | \Psi_n^{\beta} \rangle + \ldots \\ &= \frac{1}{2} \sum_{k,p,\gamma,s} q_{\alpha\beta}^{\gamma,s} \sum_{j=1}^{n_\gamma} A_{j,p}^{\gamma,k} Q_{j,k;mn}^{s,\alpha\beta} + \text{a quadratic term} \end{aligned} \tag{6}$$

Here the $q_{\alpha\beta}^{\gamma,s}$ ($s = 1, 2, \ldots$) are constants which in general include all possible mechanisms of spin-phonon interaction as well as the effects of the crystalline field. The number of q's equals the number of times Γ_γ^{*} is contained in the direct product $\Gamma_\alpha^{*} \times \Gamma_\beta$ (which is not greater than two for any of the crystallographic groups). The $Q_{j,k;m,n}^{s,\alpha\beta}$ are known matrices which depend only on the properties of the representations Γ_α and Γ_β of the group G. A method for finding these matrices was given by Koster.[5] We have not written the quadratic term in (6), because the matrix of the operator $W_{ij,k}^{\alpha\beta}$, which transforms like $\Gamma_\alpha^{*} \times \Gamma_\beta$, can be written by analogy to the matrix $V_{j,k}^{\gamma}$, after expanding the direct product in terms of irreducible representations.

When the magnetic field is switched on, the degeneracy of the levels E_α and E_β is completely removed, the quantities of practical interest are precisely the transition probabilities between the magnetic sublevels ($\sigma \to \sigma'$). Let $\mathcal{H}_{\sigma\sigma'}^{\alpha\beta}$ be the matrix elements of the spin-phonon interaction connecting the levels $\sigma \to \sigma'$ in the magnetic field. The connection between $\mathcal{H}_{\sigma\sigma'}^{\alpha\beta}$ and $\mathcal{H}_{mn}^{\alpha\beta}$ is easily found by expanding the functions $|\sigma\rangle$ in eigenfunctions $|m\rangle$:

$$\varphi_\sigma = \sum_{n} R_{n\sigma} \Psi_n, \qquad \varphi_\sigma^{*} = \sum_{m} R_{m\sigma}^{*} \Psi_m^{*}, \tag{7}$$

and then

$$\mathcal{H}_{\sigma\sigma'}^{\alpha\beta} = \sum_{m,n} R_{m\sigma}^{*} \mathcal{H}_{mn}^{\alpha\beta} R_{n\sigma'}. \tag{8}$$

Finding the unitary transformation R is equivalent to diagonalizing the matrix of the operator $V = \beta \mathbf{H} \cdot \Sigma (\mathbf{L}_i + 2\mathbf{S}_i)$ between the states $m \to n$ in the crystalline field, since the interaction of the paramagnetic particles with the external field can be treated as a perturbation. To find the general form of this matrix, following Koster,[6] we split the Hamiltonian giving the spectrum of the system of paramagnetic particles into two parts:

$$\mathcal{H} = \mathcal{H}_0 + V. \tag{9}$$

We include in $\mathcal{H}_0$ all the interactions which do not depend on the external magnetic field. The exact wave functions of $\mathcal{H}_0$ can be classified (without finding them) according to the irreducible representations of the group G. Now writing V as a sum of operators, each of which transforms according to an irreducible representation $\Gamma_\gamma \in G$:

$$V = \beta \sum_{\gamma} \sum_{k=1}^{n_\gamma} H_k^\gamma \Big(\sum_i (\mathbf{L}_i + 2\mathbf{S}_i) \Big)_k^\gamma, \tag{10}$$

we immediately write the matrix of V between the states m → n:

$$\begin{aligned} V_{mn}^{\alpha\beta} &= \beta \sum_{\gamma} \sum_{k=1}^{n_\gamma} H_k^\gamma \langle \Psi_m^\alpha \Big| \Big(\sum_i (\mathbf{L}_i + 2\mathbf{S}_i) \Big)_k^\gamma \Big| \Psi_n^\beta \rangle \\ &= \beta \sum_{\gamma, s} g_{\alpha\beta}^{\gamma, s} \sum_{k=1}^{n_\gamma} H_k^\gamma U_{k;\, mn}^{s,\, \alpha\beta}. \end{aligned} \tag{11}$$

Again the $g_{\alpha\beta}^{\gamma,s}$ are constants which include all the effects of the crystalline field and the $U_{k;mn}^{s,\alpha\beta}$ are known matrices.

The diagonalization of (11) gives the dependence of the split levels on the applied magnetic field, where the corresponding eigenfunctions are related to the initial ones (in the absence of magnetic field) by the transformation R. After finding it we calculate from (8) the general expressions for the matrix elements of $\mathcal{H}_{\sigma\sigma'}^{\alpha\beta}$, as a function of the applied magnetic field and the lattice variables. Obviously one is not always able to diagonalize (11) and find the transformation R. We shall therefore consider some practically important specific cases.

2. COMPOUNDS OF ELEMENTS OF THE IRON GROUP

In these compounds the effect of the crystalline field is usually stronger than the spin-orbit coupling. As usual we consider separately the coupling of each paramagnetic ion to the lattice; this is described by the Hamiltonian:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_Z. \tag{12}$$

We have included in $\mathcal{H}_0$ the energy of the free ion and its interaction with the crystal field. The remaining terms in the Hamiltonian can be treated as a perturbation:

$$\mathcal{H}_{LS} = \lambda \mathbf{LS}$$

is the spin-orbit interaction operator;

$$\mathcal{H}_{SS} = -\rho \Big[(\mathbf{LS})^2 + \tfrac{1}{2} (\mathbf{LS}) - \tfrac{1}{3} L (L+1) S (S+1) \Big]$$

is the spin-spin interaction operator;

$$\mathcal{H}_Z = \beta (\mathbf{L} + 2\mathbf{S}) \mathbf{H}$$

is the energy of the ion in the external magnetic field (Zeeman energy).

In most salts the crystal field can be split into two components: a strong field with cubic symmetry and a weak field with lower symmetry (usually trigonal or tetragonal). The cubic field is often produced by six water molecules located at the vertices of an octahedron whose center is occupied by the paramagnetic ion. We shall consider ions whose lowest orbital state is a singlet in a cubic field (Cr^{3+}, V^{2+}, Ni^{2+}). One can also treat Cr^{2+}, Mn^{3+}, and Cu^{2+} in this way, if the field of lower symmetry is tetragonal. For these ions the lowest orbital of the Γ_3 level in the cubic field remains a doublet, while the spin-orbit coupling has no effect whatsoever (since $\Gamma_3^* \times \Gamma_3$ does not contain Γ_4). The trigonal field splits it, leaving a $(2S+1)$-fold spin degeneracy. We shall show that for compounds containing these ions one can obtain in place of (8) a general expression for the Hamiltonian of the spin-phonon interaction, with which one can easily calculate the probabilities for individual transitions between spin states in the magnetic field.

We shall now start from the exact eigenfunctions of $\mathcal{H}_0$ and proceed exactly as one does in deriving the spin Hamiltonian.[7] The unperturbed Hamiltonian $\mathcal{H}_0$ does not depend on the spin variables, so (6) can be written in terms of constants which depend on the symmetry properties of the orbital functions alone. The total wave functions for $\mathcal{H}_0$ are of the form $\Psi^{(\gamma)} = \Psi_L^{(\gamma)} \chi_S$ where $\Psi_L^{(\gamma)}$ is an orbital wave function belonging to the irreducible representation γ of the symmetry group of the surroundings; the spin wave function χ_S belongs to the identity representation of this group, since $\mathcal{H}_0$ does not contain the spin-orbit interaction. In Eqs. (5) and (10), Γ_α and Γ_β are now the representations which correspond to the orbital wave functions (where Δ is the splitting in the cubic field). If Γ_α is a one-dimensional representation, the transformation R can be found immediately. In fact, perturbation theory for a nondegenerate state enables us to write (7) in the form

$$\varphi(\Gamma_\alpha) = \sum_n [\delta_{0n} + V_{0n}^{\alpha\beta} / (E_\alpha^0 - E_\beta^n)] \Psi_n \tag{13}$$

[where n numbers the states in Γ_β; $\Psi_0 = \Psi(\Gamma_\alpha)$]. Then

$$R_{0n}^{\alpha\beta} = \delta_{0n} + V_{0n}^{\alpha\beta} / (E_\alpha^0 - E_\beta^n); \quad V = \mathcal{H}_{LS} + \mathcal{H}_{SS} + \mathcal{H}_Z. \tag{14}$$

Since Δ is sufficiently large, we can always neglect the splitting of the level Γ_β by the field of low symmetry and by the spin-orbit interaction, i.e., we can assume $E^0_\alpha - E^0_\beta = -|\Delta|$ independent of n. In $R^{\alpha\beta}_{0n}$ the spin variables and the magnetic field appear as parameters, so in place of (8) we can write the spin-phonon interaction Hamiltonian for transitions within Γ_α:

$$\mathcal{H}_{\text{sp}} = \mathcal{H}^{\alpha\alpha}_{00} - \frac{1}{\Delta}\sum_n (V^{*\alpha\beta}_{0n}\mathcal{H}^{\beta\alpha}_{n0} + \text{c.c.}) + \frac{1}{\Delta^2}\sum_{nn'} V^{*\alpha\beta}_{0n}\mathcal{H}^{\beta\beta}_{nn'}V^{\beta\alpha}_{n'0}. \tag{15}$$

The first term $\mathcal{H}^{\alpha\alpha}_{00}$ does not depend on the spin variables and can be dropped, the second is linear in the spin variables and the third is quadratic. Obviously the third term must vanish for $S = 1/2$. For $S > 1/2$, it is often greater than the second term. This is related to the fact that the second term usually vanishes because of invariance of the states Γ_α and Γ_β under time reversal[8] ("Van Vleck annihilation"[3]).

Among the free ions of elements of the iron group one finds only S, D, and F terms. We first consider D and F terms, to which formula (15) is immediately applicable.

1) F term (Cr^{3+}, V^{2+}, Ni^{2+}); group O. In these compounds, the lowest level in the field of cubic symmetry is the orbital singlet Γ_2, which has a $(2S+1)$-fold spin degeneracy. The field of lower symmetry, which does not act on the electron spin, can give rise only to a negligible shift of the level. In first approximation the spin-orbit coupling is zero and in second approximation it is of order 1 cm^{-1}, the same order as the Zeeman energy and the spin-spin interaction. Thus the representation of the form of (10) for the operator V in (14) has the form

$$V = 2\beta \mathbf{SH} + \frac{1}{3}\rho L(L+1)S(S+1) + \sum_i \left(\lambda S_i + \beta H_i - \frac{2}{1}\rho S_i\right)L_i, \quad i = x,\ y,\ z. \tag{16}$$

The first two terms in (16) transform according to the irreducible representation Γ_1 of the cubic group (with respect to **L**), while the components of the orbital angular momentum **L** transform according to the three-dimensional representation Γ_4 of the cubic group. Since $\Gamma_2 \times \Gamma_1 = \Gamma_1$, Γ_2 $\Gamma_5 = \Gamma_4$ and $\Gamma_2 \times \Gamma_4 = \Gamma_5$, the only nonzero matrix elements from the first two terms will be within Γ_2; the third term will couple the states of Γ_2 only with those in Γ_5. Using (14), we have

$$\begin{aligned} R^{(25)}_{0n} &= \delta_{0n} - \frac{1}{|\Delta|}\sum_i \left(\lambda S_i + \beta H_i - \frac{1}{2}\rho S_i\right)\langle \Gamma_2 | L_i \ \Gamma^n_5\rangle \\ &= \delta_{0n} - \frac{1}{|\Delta|} g(\Gamma_2 \times \Gamma_5)\sum_i \left(\lambda S_i + \beta H_i - \frac{1}{2}\rho S_i\right) U_i(\Gamma_2\Gamma^n_5), \end{aligned} \tag{17}$$

where $\Delta = E^0_2 - E^n_5$, while the matrices $U_i\ (\Gamma_2\Gamma^n_5)$ have the form

$$U_x(\Gamma_2\Gamma^n_5) = (100),$$

$$U_y(\Gamma_2\Gamma^n_5) = (010), \qquad U_z(\Gamma_2\Gamma^n_5) = (001).$$

Using the symmetry properties of the normal coordinates for the complex $X - Y_6$,[9] we write the linear part of (5):

$$\mathcal{H}_{\text{sp}} = \sum_p \left(\sum_{j=1}^{3} V^{(5)}_j A^{(5)}_{j,p} + \sum_{j=1}^{2} V^{(3)}_j A^{(3)}_{j,p} + V^{(1)}_1 A^{(1)}_{1,p}\right) P_p. \tag{18}$$

This operator does not couple Γ_2 with Γ_5 ($\Gamma_2 \times \Gamma_5 = \Gamma_4$), so the second term in (15) vanishes. The matrix elements of $\mathcal{H}_{\text{sp}}$ within Γ_2 are immediately written [cf. (6)]:

$$\mathcal{H}^p_{nm} = q(\Gamma_5)\sum_{j=1}^{3} A^{(5)}_{j,p} Q^{(5)}_{j,nm} + q(\Gamma_3)\sum_{j=1}^{2} A^{(3)}_{j,p} Q^{(3)}_{j,nm} + q(\Gamma_1) A^{(1)}_{1,p} Q^{(1)}_{1,nm}. \tag{19}$$

Computations give for the matrices

$$Q^{(5)}_1 = \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad Q^{(5)}_2 = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad Q^{(5)}_3 = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix},$$

$$Q^{(3)}_1 = \begin{pmatrix} -\sqrt{3} & 0 & 0 \\ 0 & \sqrt{3} & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad Q^{(3)}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad Q^{(1)}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Finally we get from (15), (17), and (19):

$$\mathcal{H}^p = g^2(\Gamma_2 \times \Gamma_5)[\mathcal{H}^p(\Gamma_5) + \mathcal{H}^p(\Gamma_3) + \mathcal{H}^p(\Gamma_1)]/\Delta^2;$$

$$\begin{aligned} \mathcal{H}^p(\Gamma_5) = q(\Gamma_5)\, &[\alpha^2(\{S_xS_y\}A^{(5)}_{1,p} + \{S_xS_z\}A^{(5)}_{2,p} + \{S_zS_y\}A^{(5)}_{3,p}) \\ &+ 2\alpha\beta(\{S_yH_x\}A^{(5)}_{1,p} + \{S_zH_x\}A^{(5)}_{2,p} + \{S_zH_y\}A^{(5)}_{3,p}], \end{aligned}$$

$$\begin{aligned} \mathcal{H}^p(\Gamma_3) = q(\Gamma_3)\, &[\alpha^2(3S_z^2 - S(S+1) \\ &+ 2\alpha\beta(3S_zH_z - \mathbf{SH})]A^{(3)}_{1,p} \\ &+ \sqrt{3}[\alpha^2(S_y^2 - S_x^2) + 2\alpha\beta(S_yH_y - S_xH_x)]A^{(3)}_{2,p}, \end{aligned}$$

$$\mathcal{H}^p(\Gamma_1) = q(\Gamma_1)A^{(1)}_{1,p}[\alpha^2 S(S+1) + 2\alpha\beta\,\mathbf{SH}].$$

$$\{S_iS_j\} = S_iS_j + S_jS_i, \quad \{S_iH_j\} = S_iH_j + H_iS_j,$$

$$i, j = x, y, z, \ \alpha = \lambda - {}^1/_2\rho. \tag{20}$$

We have neglected terms quadratic in the external field **H**. It is easy to show that including the quadratic terms in (6) leads to an expression for $\mathcal{H}_{\text{sp}}$ which is analogous to (20), where the linear combinations $A^\alpha_{i,p}$ are replaced by quadratic expressions $(A_{ip}A_{jq})^\alpha$, which transform according to the same representation of the cubic group.

Thus the relaxation is characterized by three constants, for both first and second order processes. In [3] values of the constants $q(\Gamma_3)$ and

$q(\Gamma_5)$ are given for the Kronig–Van Vleck mechanism.[3] The completely symmetric vibration $A_{1,p}^{(1)}$ was not treated by Van Vleck, but it is clear from (20) that in the presence of the magnetic field it can give rise to relaxation transitions. In practice it seems that one can always neglect the terms in (20) which depend on the magnetic field [to order $\beta|\mathbf{H}|/(\lambda - \frac{1}{2}\rho)$] and assume that only the two constants $q(\Gamma_3)$ and $q(\Gamma_5)$ are important.

We shall discuss the case of lower symmetry for the example of the D terms.

2) D term (Cr^{2+}, Mn^{3+}). In compounds containing these ions in a cubic field, the orbital doublet Γ_3 remains lowest. Since $\Gamma_3 \times \Gamma_3$ does not contain Γ_4, the spin-orbit coupling cannot split it. A field of tetragonal symmetry splits it into two singlets, Γ_1 and Γ_3 (in the group D_{4h}).

Computations based on (15)—(19) give

$$\mathcal{H}^p = \Delta^{-2}[\mathcal{H}^p(\Gamma_1) + \mathcal{H}^p(\Gamma_3) + \mathcal{H}^p(\Gamma_4)];$$

$$\mathcal{H}^p(\Gamma_1) = q(\Gamma_1) A_p^{(1)} [\alpha^2 (S_x^2 + S_y^2) + 2\alpha\beta (S_x H_x + S_y H_y)],$$

$$\mathcal{H}^p(\Gamma_3) = q(\Gamma_3) A_p^{(3)} [\alpha^2 (S_y^2 - S_x^2) + 2\alpha\beta (S_y H_y - S_x H_x)],$$

$$\mathcal{H}^p(\Gamma_4) = q(\Gamma_4) A_p^{(4)} [\alpha^2 \{S_x S_y\} + 2\alpha\beta \{S_x H_y\}] \tag{21}$$

(where Δ is the overall splitting in the cubic field). All three constants are important. The contribution to the relaxation from the totally symmetric vibration $A_p^{(1)}$ can no longer be neglected.

For second order processes we get another constant, from the term[1] $(q(\Gamma_1')/\Delta^2)(\lambda S_z + \beta H_z - \frac{1}{2}\rho S_z)^2$. It is interesting to note that if the lowest state in the cubic field is an orbital triplet, which splits into a singlet Γ_4 and a doublet Γ_5 in the field of tetragonal symmetry, the expression for $\mathcal{H}^p$ is gotten from (21) by replacing Δ by $\delta = E_4 - E_5$ and substituting the appropriate constants. Since $\delta \ll \Delta$, we arrive at the well known fact that the spin-lattice coupling should be much stronger in this case.

Thus, in a field of tetragonal symmetry the relaxation is described by three constants for first order processes and by four constants for second order processes.

Suppose now that δ is the splitting of the lowest triplet in a field of trigonal symmetry (groups D_{3d} and C_{3v}) and $\delta \ll \Delta$. We then get for $\mathcal{H}_{sp}$ in the case of first order processes

$$\mathcal{H}^p = \frac{1}{\delta^2}(\mathcal{H}^p(\Gamma_1) + \mathcal{H}^p(\Gamma_3));$$

$$\mathcal{H}^p(\Gamma_1) = A_p^1 [\alpha^2 \{S^+S^-\} + 2\alpha\beta \{S^+H^-\}] q(\Gamma_1),$$

$$\mathcal{H}^p(\Gamma_3) = q(\Gamma_3)\{[\alpha^2 (S^+)^2 + 2\alpha\beta S^+H^+] A_p^+(\Gamma_3) + [\alpha^2 (S^-)^2 + 2\alpha\beta S^-H^-] A_p^-(\Gamma_3)\}. \tag{22}$$

Here

$$S^+ = S_x + iS_y, \qquad S^- = S_x - iS_y,$$

$$H^+ = H_x + iH_y, \qquad H^- = H_x - iH_y,$$

$$A_p^+(\Gamma_3) = A_p^{(1)}(\Gamma_3) + iA_p^{(2)}(\Gamma_3),$$

$$A_p^-(\Gamma_3) = A_p^{(1)}(\Gamma_3) - iA_p^{(2)}(\Gamma_3).$$

The relaxation is described by just two constants: $q(\Gamma_1)$ and $q(\Gamma_3)$. For second order processes a third constant appears, coming from the term

$$\mathcal{H}_{pq} = \frac{q(\Gamma_2)}{\delta^2}(A_{i,p}A_{j,q})^{(2)} [\alpha^2 (S_x^2 - S_y^2) + \alpha\beta (S_x H_x - S_y H_y)].$$

Finally, for $S = \frac{1}{2}$ (for example, Ti^{3+}) we must include the second term in (15), which is different from zero, if we take account of the Zeeman splitting of the spin levels. Then in place of (22) we have, for $S = \frac{1}{2}$,

$$\mathcal{H}^p = \alpha q(\Gamma_3) A_p^{(3)} \frac{g\beta|\mathbf{H}|}{\delta^2} S_x. \tag{23}$$

For second order processes there is again only one essential constant.

S state. For an S state, the Eqs. (15)—(19) are not valid and we must start from (2), in which the functions $V_{j,k}^{\alpha}$ are replaced by the appropriate combinations of spin variables. Using (6)—(8) one then finds the matrix elements of $\mathcal{H}_{sp}$ as a function of the field and the lattice variables. In this case one can, however, formally write the expression in terms of the spin variables, making use of the fact that a Hermitian matrix of type (8) in the space of a sublevel with spin S can be constructed using polynomials in the spin components of degree $\leq 2S$.

3. CRYSTALS CONTAINING IONS OF RARE EARTH ELEMENTS

In crystals of this type, the lattice vibrations, by modulating the crystalline field, can directly alter the direction of the magnetic moment of the rare earth ion, since the coupling between the spin and orbital moments of the electronic shell is stronger than the action of the electric field of the crystal. In contrast to (12), we must now in-

---

[1] From now on we shall drop the term $\rho(\mathbf{L}\cdot\mathbf{S})^2$ in the spin-spin interaction energy (12).

clude $\mathcal{H}_{LS}$ and $\mathcal{H}_{SS}$ in $\mathcal{H}_0$. The expression for the spin-phonon operator is gotten from (2) by replacing $V^{\alpha}_{j,k}$ by polynomials in the components of the total angular momentum **J** of degree $\leq 2J$, which transform irreducibly under the operations of the group G. We shall not dwell on this since, if we express the relative displacements in (3) in terms of the components of the deformation tensor, we arrive at the result obtained by Orbach.[10] Calculations using formulas (6)—(8) in this case give the relation between the $q^{\gamma,s}_{\alpha\beta}$ and $g^{\gamma,s}_{\alpha\beta}$ and the constants in Orbach's phenomenological Hamiltonian.[10]

I am very grateful to Prof. S. A. Al'tshuler for his interest in the work and discussion of the results, and to A. M. Leushin for useful comments.

---

[1] S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans (Electron Paramagnetic Resonance) Fizmatgiz, 1961.

[2] I. Waller, Z. Physik **79**, 370 (1932)

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

[4] R. D. Mattuck and M. W. P. Strandberg, Phys. Rev. **119**, 1204 (1960).

[5] G. F. Koster, Phys. Rev. **109**, 227 (1958).

[6] G. F. Koster and H. Statz, Phys. Rev. **113**, 445 (1959). H. Satz and G. F. Koster, Phys. Rev. **115**, 1568 (1959).

[7] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950). A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[8] E. P. Wigner, Group Theory, New York, Academic Press, 1959, p. 325.

[9] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939).

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

Translated by M. Hamermesh
308