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Method of Treating Zeeman Splittings of Paramagnetic Ions in Crystalline Fields*

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In this paper, we present an alternative method to the "spin Hamiltonian" for treating the behavior of a paramagnetic ion under the combined influence of the host crystal and an applied magnetic field. This method has the advantage of being applicable to all strengths of couplings between the paramagnetic ion and the surrounding crystal. It is applicable to free-ion S states in the same way that it applies to all other states. It gives all of the constants one needs to describe the energy level structure as a function of field as restricted by symmetry and the properties of the levels considered. The method is more general and is expected to be also more accurate than the conventional spin Hamiltonian formalism. It is illustrated by the application to the problem of the (d^5) ^6S level in a cubic crystalline environment.

I. INTRODUCTION

In this paper, we wish to consider the effect of a magnetic field on the energy levels of a paramagnetic ion in an insulating crystal. This problem has received much attention in recent years[1] and is generally handled through the use of the "spin Hamiltonian."[1,2] This method proceeds as follows.[3] A paramagnetic ion with spin degeneracy $2S+1$ and orbital angular momentum L is placed in a crystalline environment. The effect of this environment is to remove all or part of the orbital degeneracy $(2L+1)$ of the free atom state. The spin Hamiltonian describing the behavior of the lowest levels as a function of magnetic field can be derived in a simple way by the use of first and second order perturbation theory if a number of assumptions are made. The perturbation due to the crystalline field is considered larger than the fine structure of the free atom ground state but smaller than the multiplet structure of the ground configuration. Also the orbital ground state in the crystalline field has to be nondegenerate. The interaction of the paramagnetic ion with the crystal is regarded to take place through the crystalline electric field and effects due to bonding are not included in the conventional spin Hamiltonian formalism.

In the first order of perturbation theory we have the familiar $g\beta\mathbf{H}\cdot\mathbf{S}$ interaction with the external magnetic field. $\mathbf{S}$ is the spin vector of the atom, $\mathbf{H}$ is the applied magnetic field, g is the gyromagnetic ratio for an electron, and β the Bohr magneton. The second order of perturbation theory contributes additional terms in the energy which can be treated by using an effective Hamiltonian[4]

$$H_s=\mathbf{S}\cdot\mathbf{D}\cdot\mathbf{S}\cdot+\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}. \tag{1}$$

Matrix elements of this Hamiltonian have to be computed between the various $2S+1$ magnetic sublevels of a spin S. After subtracting E (the energy) from the diagonal of the resulting matrix and solving the resulting secular determinant, one obtains the energy levels of the paramagnetic ion under the combined influence of the external magnetic field and the spin orbit interaction in the crystalline environment. In the above, $\mathbf{D}$ is a tensor which comes from the second order effects of the fine-structure interaction and governs the splitting of the $2S+1$ spin degeneracy for zero magnetic field. $\mathbf{g}$ in Eq. (1) is again a tensor, a portion of which is again of the familiar form $g\beta\mathbf{H}\cdot\mathbf{S}$. Additional terms occur from second order perturbation theory involving matrix elements of the spin-orbit interaction. Simplifications in the spin Hamiltonian (1) occur because of the symmetry of the crystalline environment.

The spin Hamiltonian is generally used by assuming that $\mathbf{D}$ and $\mathbf{g}$ consist of disposable parameters which are fitted to the observed energy separations. The theory as sketched above does not apply to atoms whose free-ion state is an orbital S state. In this case, the spin Hamiltonian is constructed by the following arguments. A polynomial in the components of $\mathbf{S}$ which displays the symmetry of the crystalline environment is constructed. The order of the polynomial is less than or equal to $2S$. (Only even powers in the components of $\mathbf{S}$ need be included because of time reversal symmetry.) This polynomial has in it adjustable parameters whose number is dependent on the symmetry of the surroundings and the multiplicity of the atomic state under consideration. To this is added a tensor interaction between the magnetic field $\mathbf{H}$ and the three components of $\mathbf{S}$ with as many independent components as the symmetry permits. Again, matrix elements of

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[1] For a review article with many references to the literature, see B. Bleaney and K. W. H. Stevens, *Reports on Progress in Physics* (The Physical Society, London, 1953), Vol. 16, p. 108; K. D. Bowers and J. Owen, *Reports on Progress in Physics* (The Physical Society, London, 1955), Vol. 18, p. 304.

[2] M. H. L. Pryce, Proc. Phys. Soc. (London) **A63**, 25 (1950).

[3] In this paper and in our review of the spin Hamiltonian, we shall neglect all effects due to electric and magnetic moments of the nuclei as well as the interaction between paramagnetic ions.

[4] Vectors, tensors, matrices, and dyadics are denoted in this paper by bold-faced type.

this Hamiltonian are taken with respect to the various M_S ($-S\leq M_S\leq S$) substates of a state with spin S and the parameters are adjusted to agree with the experimental results.

As an example of this we can consider an $S=5/2$ state arising from an orbital S state in a crystalline field of cubic symmetry. The appropriate spin Hamiltonian would be

$$\alpha(S_x^4+S_y^4+S_z^4)+g\beta\mathbf{H}\cdot\mathbf{S}. \tag{2}$$

The first term is the term displaying cubic symmetry which governs the splitting in zero magnetic field and the second term is the interaction with the applied magnetic field. Only one constant is necessary to describe the interaction with the external magnetic field because of the cubic symmetry of the problem.

To derive, on the basis of perturbation theory, the spin Hamiltonian for an orbital S state would require high orders of perturbation theory.[5]

What we shall do here is to approach this problem from a somewhat different point of view. Instead of trying to explain both the zero-field splitting and the behavior of the energy levels with magnetic field in terms of perturbations of the free-ion levels, we shall start from the exact eigenstates of the paramagnetic ion in the crystalline field and describe the behavior of the ion in a magnetic field in terms of these states, taking advantage of what symmetry there may be. This method will have the advantage of making it unnecessary to consider the strength of the crystalline field relative to the spin-orbit interaction and relative to the multiplet structure as a restriction on the derivation. It will also allow us to consider orbital S states as well as all others on a par. In spirit, the treatment will be similar to that of the effect of a magnetic field on a free ion.

In a free atom, for sufficiently small magnetic fields,[6] the Hamiltonian for the interaction with the magnetic field, $\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})$, can be replaced by $g\beta\mathbf{H}\cdot\mathbf{J}$. $\mathbf{J}$ is the total angular momentum and g is the gyromagnetic ratio. This replacement can be made because the matrix elements are taken between states of a given angular momentum and because the operator $\mathbf{L}+2\mathbf{S}$ transforms like a vector. For the purpose of computing matrix elements, this operator can be replaced by an appropriate constant times any operator with the same transformation properties (i.e., $\mathbf{J}$). Once this replacement is made, the Hamiltonian matrix can be written down at once because of the ease with which matrix elements of $\mathbf{J}$ can be found. In other words, the matrix of the operator $\mathbf{L}+2\mathbf{S}$ in a manifold of states of a given total angular momentum J ($-J\leq M_J\leq J$) is just a constant times a known matrix. This is a special case of the Wigner-Eckart theorem.[7] This theorem states that the matrix of an operator, which transforms irreducibly under the full rotation group (i.e., like a spherical harmonic) taken between states of a given J, is a constant times a known matrix.[8] One can show that a somewhat similar situation exists for groups other than the full rotation group.[9] This fact is useful to describe the behavior of the energy levels of a paramagnetic ion in a crystalline field when a magnetic field is applied. To describe this behavior, more parameters will be required than in a spin Hamiltonian. The greater number of parameters is due to less restrictive physical assumptions and should give a more accurate description of the magnetic field splittings of the levels. In the next section we shall carry out this procedure.

II. METHOD

Consider an atom at some lattice site in a crystal and imagine that the symmetry of this lattice site is described by a group G.[10] Without a magnetic field the energy levels of the paramagnetic ion will have degeneracies as allowed by the symmetry of the crystal. The degeneracies will, in general, be the dimensions of the various irreducible representations of the group G. The degenerate functions belonging to a given energy level will then transform in some prescribed manner and can be chosen to be the basis for the irreducible representation of the point group in question. These eigenstates are to be considered as the exact eigenstates for the problem of the ion in the crystalline field including all interactions (spin-orbit, bonding, etc.) except for the external magnetic field. A general situation encountered is that there are sets of degenerate levels which lie close together (of the order of 1 cm^{-1} apart). These are far removed from the other levels of the ion in the crystalline field. If this is the case, when the magnetic field becomes large enough we shall have to consider the interaction between the nearby-lying levels. To illustrate the method of this section let us consider that we have an energy level E_α with eigenstates Ψ_i^α and nearby a level E_β with eigenstates Ψ_j^β. (Here the index i runs from $1\cdots n_\alpha$; the degeneracy of the level E_α, and j runs from $1\cdots n_\beta$; the degeneracy of the level E_β.) We assume further that the functions Ψ_i^α form a basis for an irreducible representation $\mathbf{\Gamma}_\alpha(R)$ and Ψ_j^β a basis for $\mathbf{\Gamma}_\beta(R)$. Thus, if R is an operator

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[5] Hutchinson, Judd, and Pope, Proc. Phys. Soc. (London) **B70**, 514 (1957).

[6] By "small" we mean that the splitting due to the magnetic field is small compared with the distance between the ground level and the next excited level.

[7] For a discussion of this theorem, see M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley and Sons, Inc., New York, 1957), p. 85.

[8] The matrix elements in the known matrix are the familiar Clebsch-Gordan (vector coupling) coefficients.

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

[10] This group must be one of the 32 crystallographic point groups. The character tables for all of the group are given in G. F. Koster, *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5, p. 173.

representing one of the symmetry operations of G, we have

$$R\Psi_i^\alpha=\sum_{m=1}^{n_\alpha}\Gamma_\alpha(R)_{mi}\Psi_m^\alpha,$$
$$R\Psi_j^\beta=\sum_{m=1}^{n_\beta}\Gamma_\beta(R)_{nj}\Psi_n^\beta. \tag{3}$$

We assume further, as mentioned above, that this pair of levels lies sufficiently far from the other energy levels of the ion in the crystalline environment; thus we need not consider the other levels when we apply the magnetic field. (That is, the magnetic splittings are small compared to the energy separation to the nearest remaining levels.)

What happens, then, when we apply a magnetic field? If H_0 is our unperturbed Hamiltonian (including *all* crystalline effects), our new Hamiltonian is

$$H_0+\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S}). \tag{4}$$

We have already chosen our states to be eigenstates of H_0 with energies E_α and E_β. We shall consider $\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})$ as the perturbation. What we must do is set up the matrix of our Hamiltonian (4), between all of the states Ψ_i^α and Ψ_j^β. This will be a square matrix of dimension $n_\alpha+n_\beta$. We can make use of the symmetry of our problem to reduce the number of independent matrix elements if we write our Hamiltonian as a sum of operators, each one of which transforms properly (irreducibly) under the group G. For the case of the crystallographic point groups, this is quite simple. If we have a single axis of more than twofold symmetry (call it the z axis), then L_z+2S_z forms a basis for one irreducible representation and[11] L_++2S_+ and L_-+2S_- either form a basis for a two-dimensional representation or are related by being bases for a pair of representations which are the complex conjugates of one another. If we have the case of one of the tetrahedral or cubic point groups, then L_x+2S_x, L_y+2S_y, and L_z+2S_z form a basis for a three-dimensional irreducible representation of these groups. If we denote by $(\mathbf{L}+2\mathbf{S})_k{}^\gamma$ that portion of $\mathbf{L}+2\mathbf{S}$ which transforms as the kth partner in the γ irreducible representation of the group G ($k=1\cdots n_\gamma$), we can then write our Hamiltonian in the form of

$$H_0+\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})=H_0+\beta\sum_\gamma\sum_k H_k{}^\gamma(\mathbf{L}+2\mathbf{S})_k{}^\gamma, \tag{5}$$

where H^γ are appropriate combinations of H_x, H_y, and H_z. For a group with only one axis which is more than twofold, we have for example,

$$H_0+\beta\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})=H_0+\beta[\tfrac{1}{2}H_+(L_-+2S_-)+\tfrac{1}{2}H_-(L_++2S_+)+H_z(L_z+2S_z)], \tag{6}$$

where

$$H_\pm=H_x\pm iH_y.$$

The terms multiplied by H_+ and H_- would belong either to one irreducible representation or to two different ones. The term multiplied by H_z would belong to yet another one. The matrix of our Hamiltonian, when written in the form of Eq. (5), can be written down at once with the number of independent constants that symmetry permits by considering each γ separately. Consider the portion of the Hamiltonian matrix which involves the interaction of the n_α states Ψ_i^α with the states Ψ_j^β. Now consider the contribution to this portion of the matrix from $\sum_k H_k{}^\gamma(\mathbf{L}+2S)_k{}^\gamma$. The number of independent constants[9,12] that this operator contributes is just the number of times the irreducible representation $\mathbf{\Gamma}_\gamma{}^*(R)$ is contained in the direct product of $\mathbf{\Gamma}_\alpha{}^*(R)$ and $\mathbf{\Gamma}_\beta(R)$. The matrix elements $\langle\Psi_i^\alpha|\sum_{k=1}^{n_\gamma}H_k{}^\gamma(\mathbf{L}+2\mathbf{S})_k{}^\gamma|\Psi_j^\beta\rangle$ can be written down at once

$$\langle\Psi_i^\alpha|\sum_{k=1}^{n_\gamma}H_k{}^\gamma(\mathbf{L}+2\mathbf{S})_k{}^\gamma|\Psi_j^\beta\rangle$$
$$=\beta g_{\gamma,1}{}^{\alpha\beta}\sum_{k=1}^{n_\gamma}H_k{}^\gamma U_{k,ij}{}^1+\beta g_{\gamma,2}{}^{\alpha\beta}\sum_{k=1}^{n_\gamma}H_k{}^\gamma U_{k,ij}{}^2+\cdots. \tag{7}$$

Here $g_{\gamma,1}{}^{\alpha\beta}$, $g_{\gamma,2}{}^{\alpha\beta}\cdots$etc. are the unknown constants. There are as many of them as the number of times $\mathbf{\Gamma}_\gamma{}^*(R)$ is contained in $\Gamma_\alpha{}^*(R)\times\Gamma_\beta(R)$. (In fact, this number is never more than two for any of the crystallographic point groups.) The $U_{k,ij}{}^1$ and $U_{k,ij}{}^2$ are matrices which can be found (for once and for all) from the properties of the representations in question.[9,13] The indices i and j run over the rows and columns of these matrices. (We should really have indices α, β, and γ on these matrices, as well, but for simplicity in writing we have suppressed them.) In a similar manner the γ contribution to the "$\alpha\alpha$" and to the "$\beta\beta$" block can be calculated. In the "$\alpha\alpha$" block, E_α must be added to the diagonal elements and in the "$\beta\beta$" block E_β must be added to the diagonal elements. This is the contribution of the Hamiltonian without a magnetic field (H_0). Since we have already chosen eigenstates of the unperturbed problem, there is no contribution from H_0 in the "$\alpha\beta$" block. If we now finally add up the contributions from each γ which appear in Eq. (5), we will have our complete Hamiltonian matrix with only the number of constants that symmetry permits.

In practice this procedure is quite simple once the matrices U are known. Since the U's are properties of the group these only need be calculated and tabulated once. In the next section, we carry out in detail a specific example to illustrate the method and in a later section compare it in detail with the spin Hamiltonian.

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[11] L_+, S_+, L_-, S_- are the familiar step-up and step-down angular momentum operators. See, for example, E. Feenberg and G. E. Pake, *Notes on the Quantum Theory of Angular Momentum* (Addison-Wesley Publishing Company, Cambridge, 1953), p. 19.

[12] Time reversal must be taken properly into account. This will be discussed in Appendix B.

[13] These matrices are discussed in Appendix A.

TABLE I. Character tables for the cubic double group (O_h). (Notation as given by Koster.[a])

	E	$\bar{E}$	$8C_3$	$8\bar{C}_3$	$3C_2 3\bar{C}_2$	$6C_4$	$6\bar{C}_4$	$6C_2' 6\bar{C}_2'$	I	$\bar{I}$	$8S_6$	$8\bar{S}_6$	$3\sigma_h 3\bar{\sigma}_h$	$6S_4$	$6\bar{S}_4$	$6\sigma_d 6\bar{\sigma}_d$
Γ_1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Γ_2	1	1	1	1	1	−1	−1	−1	1	1	1	1	1	−1	−1	−1
Γ_{12}	2	2	−1	−1	2	0	0	0	2	2	−1	−1	2	0	0	0
Γ_{25}'	3	3	0	0	−1	−1	−1	1	3	3	0	0	−1	−1	−1	1
Γ_{15}'	3	3	0	0	−1	1	1	−1	3	3	0	0	−1	1	1	−1
Γ_1'	1	1	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1
Γ_2'	1	1	1	1	1	−1	−1	−1	−1	−1	−1	−1	−1	1	1	1
Γ_{12}'	2	2	−1	−1	2	0	0	0	−2	−2	1	1	−2	0	0	0
Γ_{25}	3	3	0	0	−1	−1	−1	1	−3	−3	0	0	1	1	1	−1
Γ_{15}	3	3	0	0	−1	1	1	−1	−3	−3	0	0	1	−1	−1	1
Γ_6^+	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_7^+	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_8^+	4	−4	−1	1	0	0	0	0	4	−4	−1	1	0	0	0	0
Γ_6^-	2	−2	1	−1	0	$\sqrt{2}$	$-\sqrt{2}$	0	−2	2	−1	1	0	$-\sqrt{2}$	$\sqrt{2}$	0
Γ_7^-	2	−2	1	−1	0	$-\sqrt{2}$	$\sqrt{2}$	0	−2	2	−1	1	0	$\sqrt{2}$	$-\sqrt{2}$	0
Γ_8^-	4	−4	−1	1	0	0	0	0	−4	4	1	−1	0	0	0	0

[a] See reference 10.

III. $S=5/2$ IN A CUBIC FIELD

All we need know to carry out the procedure outlined in the last section are the transformation properties of the interacting states and the symmetry of the crystalline envirionment. The latter is standard crystallographic data and the former can be inferred from the transformation properties of the atomic state from which the crystalline state arises.[14] Consider, for example, a (d^5) ^6S state of a free ion as perturbed by a cubic crystalline field. This state has a spin of 5/2 and no orbital angular momentum. It is easy to see from the characters of the representation whose basis is the six $S=5/2$ sublevels that the sixfold degeneracy will split into a twofold and a fourfold degeneracy in a cubic environment. The four degenerate states form a basis[15] for the Γ_8^+ representation of the cubic group. The double degenerate states form a basis for the representation Γ_7^+. (The character table for the cubic double group is given in Table I.) Let us call ΔE the energy separation of these two levels.

What we must now do is to find the matrix of interaction between these six states caused by the perturbation $\mathbf{H}\cdot(\mathbf{L}+2\mathbf{S})$. The process of breaking up $\mathbf{L}+2\mathbf{S}$ into operators which transform irreducibly is trivial. L_x+2S_x, L_y+2S_y, and L_z+2S_z form a basis for the Γ_{15}' representation of the cubic group. In Eq. (5), this means that the sum over γ consists of only one term. It is now a simple matter to write down our matrix of interaction.

The first thing that we can find is the number of independent parameters we will need in the matrix. One parameter will be the energy separation ΔE between the doublet and the quartet at zero magnetic field. The remainder of the matrix will consist of a four-by-four block representing the interaction of the Γ_8^+ states with themselves, a four-by-two block representing the interaction of the Γ_8^+ states and the Γ_7^+ states and finally a two-by-two block of matrix elements connecting the Γ_7^+ states. The number of parameters in any of these blocks is the number of times $\Gamma_{15}'^{*}$ is contained in $\Gamma_8^{+*}\times\Gamma_8^+$, $\Gamma_8^{+*}\times\Gamma_7^+$ and $\Gamma_7^{+*}\times\Gamma_7^+$. For this group all characters are real and thus, from the character table, we see that

$$\begin{aligned}\Gamma_8^+\times\Gamma_8^+&=2\Gamma_{15}'+2\Gamma_{25}'+\Gamma_{12}+\Gamma_2+\Gamma_1,\\ \Gamma_8^+\times\Gamma_7^+&=\Gamma_{15}'+\Gamma_{25}'+\Gamma_{12},\\ \Gamma_7^+\times\Gamma_7^+&=\Gamma_{15}'+\Gamma_1.\end{aligned} \tag{8}$$

Thus, Γ_{15}' is contained twice in $\Gamma_8^+\times\Gamma_8^+$ and two constants are necessary to describe all terms linear in magnetic field in the four-by-four block. Similarly in the four-by-two block one constant is necessary and in the two-by-two block one constant is required. This means that, in general, four constants are required to describe the magnetic field behavior of the six levels that come from our double and fourfold degeneracy. If we include ΔE, then the number of constants is five which is to be compared with two constants in the spin Hamiltonian.

Let us now actually find the Hamiltonian matrix. In order to do this, we need to know the matrices U described in the last section. The appropriate ones are given in Tables II, III, and IV. (The details of the way these matrices were obtained are contained in Appendix B.) Making use of Eq. (7) we can now write down our complete Hamiltonian matrix. First consider the four-by-four block. This will be

$$\begin{aligned}\Delta E\mathbf{1}&+\beta g_1[H_x\mathbf{U}_x^1+H_y\mathbf{U}_y^1+H_z\mathbf{U}_z^1]\\ &+\beta g_2[H_x\mathbf{U}_x^2+H_y\mathbf{U}_y^2+H_z\mathbf{U}_z^2].\end{aligned} \tag{9}$$

Here g_1 and g_2 are constants (our $g_\gamma^{\alpha\beta}$'s of the last section), $\mathbf{1}$ is the four-by-four unit matrix, $\mathbf{U}_x^1$ and $\mathbf{U}_x^2$ etc. are the matrices contained in Table II. For the two-by-two block we have

$$\beta g_3[H_x\mathbf{U}_x^3+H_y\mathbf{U}_y^3+H_z\mathbf{U}_z^3]. \tag{10}$$

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[14] H. Bethe, Ann. Physik 3, 133 (1929).

[15] Since there are an odd number of electrons we can classify our state by the irreducible representations of the cubic double group.

TABLE II. Coupling coefficients for combining Γ_8^{+*} states with Γ_8^+ states to give states of symmetry Γ_{15}'. Matrix elements of operators transforming as Γ_{15}' (i.e., L_x+2S_x, L_y+2S_y, and L_z+2S_z) between states transforming like Γ_8^+ and Γ_8^+ are proportional to a linear combination of the two types of matrices.

$$\mathbf{U}_z^1=\frac{1}{\sqrt{2}}\begin{Vmatrix}1&0&0&0\\0&0&0&0\\0&0&0&0\\0&0&0&-1\end{Vmatrix},\qquad \mathbf{U}_z^2=\frac{1}{\sqrt{2}}\begin{Vmatrix}0&0&0&0\\0&1&0&0\\0&0&-1&0\\0&0&0&0\end{Vmatrix},$$

$$\mathbf{U}_y^1=\frac{1}{4\sqrt{2}}\begin{Vmatrix}0&-\sqrt{3}i&0&i\\\sqrt{3}i&0&-3i&0\\0&3i&0&-\sqrt{3}i\\-i&0&\sqrt{3}i&0\end{Vmatrix},\qquad \mathbf{U}_y^2=\frac{1}{4\sqrt{2}}\begin{Vmatrix}0&-\sqrt{3}i&0&-3i\\\sqrt{3}i&0&i&0\\0&-i&0&-\sqrt{3}i\\3i&0&\sqrt{3}i&0\end{Vmatrix},$$

$$\mathbf{U}_x^1=\frac{1}{4\sqrt{2}}\begin{Vmatrix}0&\sqrt{3}&0&1\\\sqrt{3}&0&3&0\\0&3&0&\sqrt{3}\\1&0&\sqrt{3}&0\end{Vmatrix},\qquad \mathbf{U}_x^2=\frac{1}{4\sqrt{2}}\begin{Vmatrix}0&\sqrt{3}&0&-3\\\sqrt{3}&0&-1&0\\0&-1&0&\sqrt{3}\\-3&0&\sqrt{3}&0\end{Vmatrix}.$$

The **U**'s are the matrices in Table III. Similarly for the four-by-two block we have

$$\beta g_4[H_x\mathbf{U}_x^4+H_y\mathbf{U}_y^4+H_z\mathbf{U}_z^4]. \tag{11}$$

The U's in matrix (11) are the four-by-two matrices from Table IV. As will be indicated further below, g_4 is a real number due to time inversion symmetry. Similarly g_1, g_2, and g_3 are real because the matrices must be Hermitian. In the above, we have chosen our zero of energy to be the doubly degenerate state. (ΔE is the energy of the fourfold degenerate states at zero field.) In Eq. (12), we show the entire Hamiltonian matrix for a magnetic field in the z direction ($H_z=H$). For simplicity we have called $\mathbf{E}_0$ the matrix of the zero-field splitting. That is, it is zero everywhere except for the first four main diagonal elements which are ΔE.

$$\mathbf{H}=\mathbf{E}_0+H\beta\begin{Vmatrix}g_1'&0&0&0&0&g_4'\\0&g_2'&0&0&0&0\\0&0&-g_2'&0&0&0\\0&0&0&-g_1'&g_4'&0\\0&0&0&g_4'&-g_3'&0\\g_4'&0&0&0&0&g_3'\end{Vmatrix}. \tag{12}$$

Here $g_1'=g_1/\sqrt{2}$; $g_2'=g_2/\sqrt{2}$; $g_3'=g_3/\sqrt{2}$; and $g_4'=g_4/\sqrt{2}$. This matrix as it stands gives the behavior of the six levels as a function of magnetic field. This matrix is valid under the assumption that the magnetic field is sufficiently small so that we can neglect the interaction due to the external magnetic field with states coming from free-atom states higher than the ^6S of the d^5 configuration. This is quite a valid assumption in most paramagnetic salts. These higher levels generally lie of the order of thousands of wave numbers higher than

TABLE III. Coupling coefficients for combining Γ_7^{+*} states with Γ_7^+ states to give states of symmetry Γ_{15}'. Matrix elements of operators transforming as Γ_{15}' (i.e., L_x+2S_x, L_y+2S_y, and L_z+2S_z) between states transforming like Γ_7^+ and Γ_7^+ are proportional to the matrices.

$$\mathbf{U}_z^3=\frac{1}{\sqrt{2}}\begin{Vmatrix}-1&0\\0&1\end{Vmatrix},\qquad \mathbf{U}_y^3=\frac{1}{\sqrt{2}}\begin{Vmatrix}0&i\\-i&0\end{Vmatrix},\qquad \mathbf{U}_x^3=\frac{1}{\sqrt{2}}\begin{Vmatrix}0&-1\\-1&0\end{Vmatrix}.$$

TABLE IV. Coupling coefficients for combining Γ_8^{+*} states with Γ_7^+ states to give states of symmetry Γ_{15}'. Matrix elements of operators transforming as Γ_{15}' (i.e., L_x+2S_x, L_y+2S_y, and L_z+2S_z) between states transforming like Γ_8^+ and Γ_7^+ are proportional to the matrices.

$$\mathbf{U}_z^4=\frac{1}{\sqrt{2}}\begin{Vmatrix}0&1\\0&0\\0&0\\1&0\end{Vmatrix},\qquad \mathbf{U}_y^4=\frac{1}{2\sqrt{2}}\begin{Vmatrix}i&0\\0&-\sqrt{3}i\\-\sqrt{3}i&0\\0&i\end{Vmatrix},\qquad \mathbf{U}_x^4=\frac{1}{2\sqrt{2}}\begin{Vmatrix}1&0\\0&-\sqrt{3}\\\sqrt{3}&0\\0&-1\end{Vmatrix}.$$

TABLE V. Polynomials in the components of $\mathbf{S}$ transforming under rotations like substates M of a given angular momentum L.

$L=1$	$M=1$	$(-1/\sqrt{2})S_+$
	$M=0$	S_z
$L=2$	$M=2$	$\frac{1}{2}S_+^2$
	$M=1$	$-\frac{1}{2}S_+(2S_z+1)$
	$M=0$	$[3/(6)^{\frac{1}{2}}](S_z^2-\mathbf{S}^2)$
$L=3$	$M=3$	$-\frac{1}{2}(1/\sqrt{2})S_+^3$
	$M=2$	$[(3/4)^{\frac{1}{2}}]S_+^2(1+S_z)$
	$M=1$	$(1/30)^{\frac{1}{2}}S_+[-3+\frac{3}{2}\mathbf{S}^2-(15/2)S_z-(15/2)S_z^2]$
	$M=0$	$(1/10)^{\frac{1}{2}}(5S_z^3-3S_z\mathbf{S}^2+S_z)$
$L=4$	$M=4$	$\frac{1}{4}S_+^4$
	$M=3$	$\frac{1}{4}(1/\sqrt{2})S_+^3(-6-4S_z)$
	$M=2$	$\frac{1}{2}[1/(7)^{\frac{1}{2}}]S_+^2(9-S^2+7S_z^2+14S_z)$
	$M=1$	$[1/(56)^{\frac{1}{2}}]S_+(-6+3\mathbf{S}^2+6S^2S_z-19S_z-21S_z^2-14S_z^3)$
	$M=0$	$[1/(280)^{\frac{1}{2}}](35S_z^4+25S_z^2-30S_z^2\mathbf{S}^2+3\mathbf{S}^4-6\mathbf{S}^2)$
$L=5$	$M=5$	$-\frac{1}{4}(1/\sqrt{2})S_+^5$
	$M=4$	$\frac{1}{4}[1/(5)^{\frac{1}{2}}]S_+^4(10+5S_z)$
	$M=3$	$(5/4)[1/(90)^{\frac{1}{2}}]S_+^3(-24+\mathbf{S}^2-27S_z-9S_z^2)$
	$M=2$	$[(5/12)^{\frac{1}{2}}]S_+^2(6-\mathbf{S}^2-\mathbf{S}^2S_z+12S_z+9S_z^2+3S_z^3)$
	$M=1$	$[(5/336)^{\frac{1}{2}}]S_+(-12-\mathbf{S}^4+8\mathbf{S}^2+14\mathbf{S}^2S_z+14\mathbf{S}^2S_z^2-42S_z-63S_z^2-42S_z^3-21S_z^4)$
	$M=0$	$\frac{1}{3}[(1/56)^{\frac{1}{2}}](12S_z-50\mathbf{S}^2S_z+15\mathbf{S}^4S_z-70\mathbf{S}^2S_z^3+105S_z^3+63S_z^5)$

the ${}^6S$. We see that the symmetry properties of the Hamiltonian and of the states in question have greatly restricted the number of independent constants in the six-by-six matrix.

IV. COMPARISON WITH THE SPIN HAMILTONIAN

The spin Hamiltonian for our specific example was given by (2). The general problem of finding spin Hamiltonians is somewhat facilitated if one has available polynomials in S_+, S_-, and S_z which transform in the same way under the full rotation group as the spherical harmonics. In Table V, we give all polynomials of order less than six which transform as the various sublevels of angular momentum. These will be useful later in this section and were obtained by the process described by Rose.[16] Using this table and knowing the combination of spherical harmonics for $L=4$ which are invariant under the cubic group,[1] the spin Hamiltonian (2) can be rewritten in the more convenient form.

$$g\beta\mathbf{H}\cdot\mathbf{S}+\alpha\{(1/20)[35S_z^4-30\mathbf{S}^2S_z^2+25S_z^2-6\mathbf{S}^2+3\mathbf{S}^4]+\tfrac{1}{8}[S_+^4+S_-^4]\}. \quad (13)$$

This Hamiltonian as it stands has only 2 parameters as compared to the 5 parameters obtained in the last section. Both methods give one parameter to describe the zero-field splittings; but whereas the method of this paper gives four constants describing terms linear in the applied field, the method of the spin Hamiltonian gives only one. The physical reason for this difference lies mainly in the fact that the spin Hamiltonian uses eigenfunctions which are linear combinations of the magnetic sublevels of a spin 5/2. It does not allow for the possibility that the fourfold degenerate states are modified differently than the double degenerate ones. If this were the case, as we shall see in detail later, the splitting of the fourfold degeneracy in a magnetic field would be unrelated to the splitting of the double degeneracy. In the present method, only the symmetry properties of the states enter into the calculation and the wave functions, in general, will have admixtures from the higher lying states of the free atom and from states of neighboring atoms. This admixture gives the present method the necessary flexibility. After having obtained the most general answer from group theory, we shall show what terms have to be added to the spin Hamiltonian to obtain formally the same answers as in the last section.

It is clear that we can always reproduce any Hermitian six-by-six Hamiltonian matrix by taking the matrix elements in a space of substates of spin 5/2 of polynomials in the components of S_x, S_y, and S_z up to and including order 5. Without destroying the over-all symmetry, we can add to the Hamiltonian (13) additional terms which are linear in the magnetic field. If we multiply H_x by any polynomial which transforms like x under the operations of the cubic group, and add it to H_y and H_z multiplied by polynomials trans-

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[16] See reference 7, p. 144: In order to obtain Rose's $I_{LM}(\mathbf{S})$ we must multiply the entries in the table by $(4\pi)^{-\frac{1}{2}}[L!(2L+1)!!]^{\frac{1}{2}}$, where $(2L+1)!!\equiv 1\times 3\times 5\cdots\times(2L+1)$. In order to obtain negative M for a given L, take the entry in the table and (1) change S_+ to S_-; (2) for odd L, change the sign of odd powers of the components of $\mathbf{S}$ for odd M and the sign of even powers of the components of $\mathbf{S}$ for even M; (3) for even L, change the sign of odd powers of the components of $\mathbf{S}$ for even M and the sign of even powers of the components of $\mathbf{S}$ for odd M.

forming like y and z, respectively,[17] we shall be able to generalize the spin Hamiltonian in the desired way. For simplicity, consider a magnetic field in the z direction. If we multiply H_z by any polynomial of the third or fifth order which transforms like z under the operations of the cubic group, we shall have terms which we can add to the spin Hamiltonian. For the cubic polynomial we can use a term of the type $L=3$, $M=0$ (see Table V)

$$g_0{}^3\beta H_z[S_z{}^3-\tfrac{3}{5}\mathbf{S}^2S_z+\tfrac{1}{5}S_z]. \tag{14}$$

For the terms of the fifth order we can construct, in two ways, combinations of the M levels of $L=5$ which transform like z. One is $L=5$, $M=0$. This contributes a term

$$g_0{}^5\beta H_z[63S_z{}^5+S_z{}^3(-70\mathbf{S}^2+105) +S_z(12-50\mathbf{S}^2+15\mathbf{S}^4)]. \tag{15}$$

In addition a combination of ($L=5$, $M=4$) and ($L=5$, $M=-4$) contributes an additional term

$$g_4{}^5\beta H_z\tfrac{3}{2}(35)^{\frac{1}{2}}\{(S_+{}^4+S_-{}^4)S_z+2(S_+{}^4-S_-{}^4)\}. \tag{16}$$

The three terms (14), (15), and (16) should be added to the spin Hamiltonian (13). The Hamiltonian will then have the most general form that it can have for the symmetry of the problem and the states under consideration. This generalized spin Hamiltonian now also has 5 constants and corresponds to the group-theoretical matrices discussed in the last section.

It is instructive to find the relation between the constants of Sec. III and the constants of the extended spin Hamiltonian of this section. This is easily done by writing down the matrix of the Hamiltonian obtained by adding (13), (14), (15), and (16) in a basis of the sublevels of $S=5/2$. By doing this first for $H=0$, we can obtain the relation between α in the Hamiltonian (13) and the separation ΔE of the fourfold and twofold degeneracies. The matrix of Hamiltonian (13) for $H=0$ is

$$\alpha\begin{Vmatrix} 3 & 0 & 0 & 0 & 3\sqrt{5} & 0 \\ 0 & -9 & 0 & 0 & 0 & 3\sqrt{5} \\ 0 & 0 & 6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 6 & 0 & 0 \\ 3\sqrt{5} & 0 & 0 & 0 & -9 & 0 \\ 0 & 3\sqrt{5} & 0 & 0 & 0 & 3 \end{Vmatrix}. \tag{17}$$

By finding the roots of this matrix and equating their difference to ΔE, we obtain

$$\Delta E=18\alpha. \tag{18}$$

The matrix of the terms linear in the magnetic field from (13), (14), (15), and (16) between the various M_S levels of $S=5/2$ yields

$$\beta H\begin{Vmatrix} \frac{5}{2}g+3g_0{}^3+30g_0{}^5 & 0 & 0 & 0 & (30\sqrt{7})g_4{}^5 & 0 \\ 0 & \frac{3}{2}g-(21/5)g_0{}^3-150g_0{}^5 & 0 & 0 & 0 & -(30\sqrt{7})g_4{}^5 \\ 0 & 0 & \frac{1}{2}g-(12/5)g_0{}^3+300g_0{}^5 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2}g+(12/5)g_0{}^3-300g_0{}^5 & 0 & 0 \\ (30\sqrt{7})g_4{}^5 & 0 & 0 & 0 & -\frac{3}{2}g+(21/5)g_0{}^3+150g_0{}^5 & 0 \\ 0 & -(30\sqrt{7})g_4{}^5 & 0 & 0 & 0 & -\frac{5}{2}g-3g_0{}^3-30g_0{}^5 \end{Vmatrix}. \tag{19}$$

In comparing the matrices (19) and (12), one has to be careful. In matrix (19), just the 6 substates of a spin of 5/2 have been used as basis functions, whereas in matrix (12) two sets of functions have been used which transform irreducibly under the cubic group. To facilitate a comparison, we can take linear combinations of the functions used in matrix (12) so that they transform like the six sublevels of a spin 5/2. This linear combination can be found by the method described in Appendix C. The corresponding transform of the matrix (12) can then be compared, element by element, with the matrix (19). The relations between the two sets of constants are then found to be as follows:

$$\begin{aligned} g_1{}'&=-(11/6)g-(16/5)g_0{}^3-50g_0{}^5-10(35)^{\frac{1}{2}}g_4{}^5,\\ g_2{}'&=\tfrac{1}{2}g-(12/5)g_0{}^3+300g_0{}^5,\\ g_3{}'&=\tfrac{5}{6}g-4g_0{}^3-130g_0{}^5+10(35)^{\frac{1}{2}}g_4{}^5,\\ g_4{}'&=-(\tfrac{2}{3}\sqrt{5})g+(\sqrt{\tfrac{1}{5}})g_0{}^3+(20\sqrt{5})g_0{}^5+(20\sqrt{7})g_4{}^5. \end{aligned} \tag{20}$$

Next, consider the eigenvalues of the Hamiltonian matrix (12) and assume that the magnetic field is weak enough so that the splittings are much smaller than ΔE. It is then clear from matrix (12) that we can

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[17] The polynomial, because of time reversal, must contain only odd powers of the components of $\mathbf{S}$.

neglect the off-diagonal terms in $g_4'\beta H$ (since these connect states separated by ΔE). This means that out of the fourfold degeneracy, four states emerge linear with H. Their slopes are $\pm g_1'\beta$ and $\pm g_2'\beta$. Out of the twofold degeneracy, two states with slopes $\pm g_3'\beta$ emerge. Thus, from a measurement of the three low-field slopes, the constants g_1' through g_3' can be found. The ordinary spin Hamiltonian with $g_0{}^3=g_0{}^5=g_4{}^5=0$ would predict a relation between the three slopes. They would be [see Eq. (20)]: $\pm(11/6)g\beta$, $\pm\frac{1}{2}g\beta$, and $\pm\frac{5}{6}g\beta$. Thus, the present method gives three independent low-field slopes, whereas the conventional spin Hamiltonian gives three interrelated slopes with only one adjustable parameter, i.e., g.

Next consider high fields. By this we mean fields so large that the splitting is greater than ΔE, the zero-field splitting. We can now neglect the matrix $\mathbf{E}_0$ in Eq. (12) and the slopes for high fields are easily found. The two states which have slopes $\pm g_2'$ at low fields continue all the way to high fields linear in the field with the same slope. Solving the secular equation obtained from Eq. (12) shows that the remaining four states have slopes

$$\pm\tfrac{1}{2}\beta\{g_1'+g_3'\pm[(g_1'-g_3')^2+4g_4'^2]^{\frac{1}{2}}\}. \tag{21}$$

As mentioned, from low-field measurements g_1', g_2', and g_3' could be found. By measuring one slope at high fields, excluding the one described by g_2', the last parameter g_4' can be obtained and thus the entire energy spectrum as a function of magnetic field. The ordinary spin Hamiltonian would predict [see Eq. (19) and set $g_0{}^3$, $g_0{}^5$, and $g_4{}^5$ equal to zero] that the high-field slopes should be uniquely determined in terms of one g and should have values $\pm\frac{5}{2}g\beta$, $\pm\frac{3}{2}g\beta$, and $\pm\frac{1}{2}g\beta$. We can also see from Eq. (20) that as we successively allow $g_0{}^3$, $g_0{}^5$, and $g_4{}^5$ to take on values different from zero, we gradually eliminate the relations that the spin Hamiltonian puts between the independent constants on the left-hand side.

In this way we see that the method of this paper, while still limiting the number of parameters necessary to determine the behavior of the energy levels as a function of field, does give more freedom than the ordinary spin Hamiltonian. It gives, however, only that freedom which the symmetry and the nature of the interacting states permit.

V. CONCLUSION

The method of this paper provides a means of treating the behavior of paramagnetic ions in a crystalline environment which offers advantages over the ordinary spin Hamiltonian. It is not restricted in its applicability to assumptions about the strength of the crystalline field. Since the considerations used are essentially symmetry arguments, no specific assumptions need be made about the detailed nature of the wave functions of the paramagnetic ions. All effects due to admixture of higher states of the atom as well as contributions due to binding with neighboring nonmagnetic ions are automatically included. It can be applied to levels arising from orbital S states of the free atom in the same way that it can be applied to all other states. The U matrices necessary to carry out this method are dependent only on the symmetry group of the lattice site and the transformation properties of the corresponding free-ion wave functions. Their elements have many features of the Clebsch-Gordan coefficients. Therefore, they are quantities which should find wide applicability in problems where matrix elements of operators with definite transformation properties are required as well as in problems concerning the coupling of states of various symmetry types. In the near future, the authors hope to publish more complete tables of these coefficients for all of the point groups of interest.[18]

The disadvantage of the method lies in the difficulty of fitting experimental data to the larger number of parameters. In the case considered in this paper, this does not seem too formidable but in other cases of lower symmetry this may be more difficult. That the spin Hamiltonian approach has met with great success as it stands is evidenced by the tables of parameters published by Bowers and Owen.[1] It should be kept in mind, however, that much of the fitting of experimental paramagnetic resonance data has been carried out in a very narrow range of frequencies. As accurate and more extensive experimental data become available, it will very probably become necessary to use the present approach to adequately describe the experimental findings. A possible example for the inadequacy of the conventional spin Hamiltonian of the form (2) is given by Müller[19] who investigates the ${}^6S$ state of Fe^{+++} in $\mathrm{SrTiO_3}$ crystals. He has already found discrepancies of five to ten percent when measuring at only one wavelength of 3.2 cm. There still remains, of course, the more fundamental problem of interpreting the additional constants of this extended parametrization in terms of the many-electron wave functions of the paramagnetic ion in the crystalline field.

APPENDIX A

The matrices $\mathbf{U}$ which we use in the text have the following meaning: Imagine two sets of functions $\varphi_i{}^{\alpha *}$ and $\varphi_j{}^\beta$. The first set forms a basis for the irreducible representation $\Gamma_\alpha{}^*$ and the second set a basis for the irreducible representation Γ_β of the group G. If we were to take the $n_\alpha n_\beta$ products of these functions, $\varphi_i{}^{\alpha *}\varphi_j{}^\beta$, we would have a set of functions which form a basis for the representation $\Gamma_\alpha{}^*\times\Gamma_\beta$. In general, this representation will be reducible and we can ask what linear combinations of the products transform ir-

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[18] For other coupling coefficients for the cubic group, see Y. Tanabe and S. Sugano, J. Phys. Soc. Japan **9**, 753 (1954).

[19] K. A. Müller, Helv. Phys. Acta **31**, 173 (1958).

reducibly under the group G. Let us imagine that we wanted those linear combinations that transform according to the irreducible representation $\Gamma_\gamma{}^*$. Call these linear combinations $\Psi_k{}^\gamma(k=1\cdots n_\gamma)$.

$$\Psi=\sum_{i,j} U_{k,ij}\varphi_i{}^{\alpha*}\varphi_j{}^\beta. \tag{A1}$$

In the linear combination the $U_{k,ij}$ are those coefficients that give the new states of the proper symmetry. (They are the elements of the unitary matrix which reduces the direct product prepresentation $\Gamma_\alpha{}^*\times\Gamma_\beta$.) It may happen that there is more than one way to reduce the direct product. By this we mean that one may be able to construct two or more sets of n_γ functions which form a basis for $\Gamma_\gamma{}^*$. In such cases, we must put an additional index on the U's to specify which set we mean. Thus, we would have

$$\begin{aligned}\Psi_k{}^{\gamma,1}&=\sum_{i,j} U_{k,ij}{}^1\varphi_i{}^{\alpha*}\varphi_j{}^\beta,\\ \Psi_k{}^{\gamma,2}&=\sum_{i,j} U_{k,ij}{}^2\varphi_i{}^{\alpha*}\varphi_j{}^\beta,\\ \Psi_k{}^{\gamma,3}&=\sum_{i,j} U_{k,ij}{}^3\varphi_i{}^{\alpha*}\varphi_j{}^\beta.\end{aligned} \tag{A2}$$

We shall have as many sets of functions $\Psi_k{}^\gamma$ as the number of times $\Gamma_\gamma{}^*$ is contained in $\Gamma_\alpha{}^*\times\Gamma_\beta$. This number is obtained at once from the character table of G. In a paper by one of the authors,[9] it was shown that the first $c_\gamma n_\gamma$ rows of the matrix reducing the direct product (c_γ=number of times $\Gamma_\gamma{}^*$ is contained in $\Gamma_\alpha{}^*\times\Gamma_\beta$, n_γ=dimension of representation $\Gamma_\gamma{}^*$) are simply related to the matrix elements of operators which form a basis for Γ_γ.

The coefficients $U_{k,ij}$ are, of course, exactly analogous to the Clebsch-Gordan (or vector coupling, or Wigner $3j$) coefficients for the full rotation group. In this case, the fact that the product of two representations is being reduced can be expressed by saying that two angular momenta are coupled to give a third. This is a somewhat simpler case than the corresponding problem in finite groups since there is, for any two angular momenta, only one way of coupling them to give a third angular momentum. In our case, there may be more than one independent way of coupling the two sets of states.

In reference 9 a method is given by which the U's can be calculated. By taking the sum over all group elements of the product of matrix elements for the three representations considered, we obtain

$$\sum_R \Gamma_\alpha{}^*(R)_{mi}\Gamma_\beta(R)_{nj}\Gamma_\gamma(R)_{pk}. \tag{A3}$$

For any choice of m, n, and p one obtains a possible matrix element (outside of a multiplicative constant) of $U_{k,ij}$. (For some choices of m, n, and p one may get zero for all i, j, and k. This cannot be true for all choices if $\Gamma_\gamma{}^*$ is contained in $\Gamma_\alpha{}^*\times\Gamma_\beta$.) If $\Gamma_\gamma{}^*$ is contained more than once, a new m, n, and p is chosen until a new set of numbers linearly independent with the first set is obtained. Consider these two sets of numbers as vectors. Orthonormalizing them by linear combinations results in $U_{k,ij}{}^1$ and $U_{k,ij}{}^2$ of Eq. (A2).

APPENDIX B

The matrices $U_{k,ij}$ for reducing the products of representations of a group depend, of course, on the exact form of the representation chosen. In the case of the Clebsch-Gordan coefficients, we have the full rotation group. It is standard to specify the representations by choosing as a basis eigenstates of the z component of the angular momentum operator. For the point groups it is not obvious what kinds of bases should be chosen. In the remainder of this appendix, we shall discuss the choices made for the example in the text.

The $\Gamma_8{}^+$ representation can be considered to have as a basis the four M_S levels of a spin 3/2. This is what we did. We chose the form of the matrices in this representation to be as in Rose.[7] The $\Gamma_7{}^+$ representation can be considered as the direct product of the one-dimensional representation Γ_2 and the two-dimensional representation $\Gamma_6{}^+$ which has as a basis the two M_S levels of $S=1/2$ ($\Gamma_7{}^+=\Gamma_2\times\Gamma_6{}^+$). We chose again $\Gamma_6{}^+$ to be the $D_{1/2}$ of Rose.[7] For the representation $\Gamma_{15}{}'$ we chose, as a basis, functions which transform like the coordinates x, y, and z (except that we took them even under inversion). So that there can be no misunderstanding we give the matrix representing a rotation about the $+z$ axis clockwise by 90°:

$$\left\|\begin{matrix}0 & -1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{matrix}\right\|, \tag{B1}$$

and the matrix representing a rotation clockwise through 90° about the positive y axis:

$$\left\|\begin{matrix}0 & 0 & 1\\ 0 & 1 & 0\\ -1 & 0 & 0\end{matrix}\right\|. \tag{B2}$$

By carrying out the process of reference 9 [see Eq. (A2)], we obtained the matrices given in Tables II, III, and IV. (The choices of m, n, and p were 113 and 223 in Table II; 113 in Table III; and 113 in Table IV.)

A word should be said here about time reversal. The representations $\Gamma_8{}^+$ and $\Gamma_7{}^+$ have the property that they are equivalent to their complex conjugates but cannot be made real.[20] For these, the basis is chosen[7] so that for $\Gamma_8{}^+$

$$K\Psi_i{}^\alpha=(-1)^{\frac{3}{2}+i}\Psi_{-i}{}^\alpha. \tag{B3}$$

In Eq. (B3), i runs over the values 3/2, 1/2, −1/2, and −3/2 instead of over the values 1, 2, 3, and 4, respectively. K is the Wigner time-reversal operator. For the representation $\Gamma_7{}^+$,

$$K\Psi_j{}^\beta=(-1)^{\frac{1}{2}+j}\Psi_{-j}{}^\beta. \tag{B4}$$

In Eq. (B4), j takes on the values 1/2 and −1/2 rather than the values 1 and 2. The operator $\mathbf{L}+2\mathbf{S}$ goes into

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[20] E. Wigner, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. p. 546 (1932).

its negative under time inversion. Consider then, for example, the matrix element

$$\begin{aligned}&\langle\Psi_1{}^\alpha|L_z+2S_z|\Psi_1{}^\alpha\rangle\\&\quad=\langle K\Psi_1{}^\alpha|K(L_z+2S_z)K^{-1}|K\Psi_1{}^\alpha\rangle^*\\&\quad=-(-1)^{\frac{3}{2}+\frac{3}{2}}(-1)^{\frac{3}{2}+\frac{3}{2}}\langle\Psi_4{}^\alpha|L_z+2S_z|\Psi_4{}^\alpha\rangle\\&\quad=-\langle\Psi_4{}^\alpha|L_z+2S_z|\Psi_4{}^\alpha\rangle.\end{aligned}\tag{B5}$$

We see that the matrices $\mathbf{U}^1$ and $\mathbf{U}^2$ in Table II have this property so that time reversal does not influence the fact that we have two constants g_1 and g_2. (If, on the other hand, L_z+2S_z were a Hermitian operator, even under time inversion all matrix elements of all components of this operator between these states would vanish, i.e., $g_1=g_2=0$.) In a similar way, we can see that time reversal does not influence the number of constants in the two-by-four block or in the two-by-two block. It does, however, cause g_4 to be real. (g_1, g_2, and g_3 are obviously real since we are dealing with a Hermitian operator.)

In general, time reversal can influence the number of independent constants necessary to determine matrix elements of symmetric operators. Arguments of the type given in Eq. (B5) will determine how the number of constants is influenced.

APPENDIX C

The basis for the sublevels of spin 5/2 was chosen to be that given by Rose.[7] The unitary matrix which transforms this basis to two sets of functions transforming like $\Gamma_8{}^+$ and $\Gamma_7{}^+$ can be found by the method given in reference 9. Performing the corresponding similarity transformation of the Hamiltonian matrix (12) allows one to identify terms in the transformed matrix (12) with those of (19) and thus to get the relations between the constants.

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Conductivity of Grain Boundaries in Grown Germanium Bicrystals

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The conduction of current in the grain boundary of a grown germanium bicrystal has been studied as a function of doping. For all samples, the behavior shows only a small temperature dependence from 2–300°K. The conduction in the grain boundary is ohmic if no secondary effects are introduced by conduction in the bulk material. Samples with no doping and with *n*-type, *p*-type, or copper doping are all characterized by having a resistivity of about 3000 to 11 000 ohms per square. The lack of a strong dependence on doping indicates that the grain boundary behavior is not due to the segregation of impurities at the boundary.

The nonohmic character for current flow perpendicular to grain boundaries in *n*-type germanium was found in early work on polycrystalline material.[1,2] This means that the grain boundary is a *p*-type layer, forming an *n–p–n* structure. In *p*-type germanium, this nonohmic behavior disappears but photoelectric measurements show that the grain boundary now acts as a p^+-type layer.[3] The *p*-type nature of the grain boundary was confirmed by Tweet[4] using measurements of the Hall effect for current flow in the grain boundary sheet of gold-doped germanium bicrystals. A partial explanation of this behavior was given by Taylor, Odell, and Fan[5] in terms of the formation of a double Schottky barrier about the grain boundary due to charges in surface states which may arise either from lattice misfit or segregation of acceptor type impurities at the boundary. The misfit at the grain boundary, according to the model proposed by Read[6] for dislocations and extended to grain boundaries by Mataré[7] causes "dangling bonds." These dangling bonds are able to pick up electrons in a lower energy state until the energy lost by adding an electron is compensated by the energy increase due to electron repulsion. On the other hand, the possibility that the behavior may be due to impurities is present in Tweet's experiment where gold is an acceptor that may not completely deionize at the lowest temperatures used. In other cases the *p*-type layer has been attributed to the segregation at the boundary of copper which is an acceptor.

In a study of the effect of impurities on grain boundary behavior, measurements of the current in the grain boundary were made for a variety of crystal dopings. The work was performed on carefully oriented bicrystals[8] grown by the vertical pulling technique with [100] seeds symmetrically tilted about the [010] axis at

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