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SPLITTING OF ATOMIC TERMS WITH INTEGER TOTAL ANGULAR MOMENTUM IN A MAGNETIC CRYSTAL

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A method is proposed for finding the degeneracy caused by magnetic symmetry. The method is used to examine the nature of the splitting of atomic terms in a magnetic crystal for all cases of magnetic symmetry, under the assumption that the total angular momentum of the atom is integral. The results are compared with the splitting of atomic terms in a nonmagnetic crystal. It is found that the magnetic interaction in the crystal does not always remove the degeneracy of the atomic energy levels completely. It is shown that the results obtained are applicable to finding the splitting of terms of an atom in a nonmagnetic crystal which is placed in a magnetic field.

1. The field due to the other atoms of the crystal acts on an atom located in a crystal. This field has a definite symmetry which depends on both the crystal symmetry and on the position of the atom under consideration. The symmetry of the crystal field is a subgroup of the symmetry class of the crystal. The crystalline field can be treated as a perturbation which splits the energy levels of the unperturbed atom. This splitting is completely dependent on the symmetry of the crystal field at the point where the atom is located.

The question of splitting of atomic terms under the action of the crystalline field was treated by Bethe.¹ If we assume that the perturbation due to the crystal field is so small that the spin-orbit coupling in the atom is not broken down, we can start from a state of the free atom which is given by its total angular momentum J and its parity. Under the influence of the crystal field, the symmetry of the atom is reduced, which leads to partial or complete lifting of the degeneracy of the

atomic state. To find this splitting we must expand the irreducible representation of the symmetry group of the free atom in irreducible representations of the symmetry group of the crystal field. The irreducible representation of the symmetry group of the free atom (spherical symmetry) gives the term of the unperturbed atom, while the irreducible representations of the symmetry group of the crystal field which are found in the expansion give the components in the splitting of the term.

We must however make one important reservation. The free atom is symmetric under time inversion. If the crystal field is purely electric, it is also symmetric under the time inversion R . Then the perturbed atom must also possess this symmetry. One might think that the symmetry with respect to R could be taken into account in the usual scheme of expansion in irreducible representations by assuming that the symmetry group of the crystal field also includes the time inver-

sion. However this approach is incorrect. The point is that time inversion results in the replacement of the wave functions by their complex conjugates (when the spin is omitted). Complex conjugation is not a linear operation and, consequently, the symmetry group including the time inversion can have nonlinear representations in the basis of the wave functions. For this reason the effect of the time inversion on the splitting of atomic terms is treated outside the usual scheme:² one first treats the term splitting omitting the symmetry under the time inversion R , and then counts the two nonequivalent complex conjugate irreducible representations not as two different states, but as a single state with a degeneracy twice as great as the dimensionality of the representations.*

2. In the present paper the treatment of the splitting of atomic terms by a crystal field is extended to the case of magnetic crystals (ferromagnetics and antiferromagnetics). In this case an atom in the crystal is acted on not only by an electric field but also by the magnetic field due to the other atoms in the crystal. Thus the symmetry group of the crystal field is not one of the 32 crystallographic classes, but is a magnetic symmetry group (magnetic class).^{3,4} Since the symmetry of the free atom contains all the elements of the magnetic classes, the symmetry of the perturbed atom will coincide with the symmetry of the field of the magnetic crystal.

The magnetic classes are of two types.³ The first consists of those magnetic classes which coincide with the 32 crystallographic classes. The term splitting in a field with such a symmetry can be found as in reference 1. The results will be different, however, in that the components in the split term, which correspond to nonequivalent complex conjugate irreducible representations, should be counted as different, and not as coincident, as is the case when there is symmetry with respect to R .

The remaining 58 magnetic classes contain symmetry elements which are products of "rotations"† A with the time inversion R , but do not contain R itself. It is easily understood that, because of the time inversion, an operation like RA transforms the wave functions nonlinearly.

*This is correct if the wave functions satisfy a Schrödinger equation, i.e., if the spin is not included. When the spin is included, the same result is found if the angular momentum of the atom is integral.¹

†By "rotations" we always understand both true rotations and rotation-reflections which are a product of a true rotation and the space inversion.

The usual procedure for finding the splitting of atomic terms is therefore not applicable in this case.

The splitting of atomic terms when the crystal field has the symmetry of one of the 58 magnetic classes will differ essentially from the splitting in the case of the crystallographic classes.

3. We now formulate the problem. A state of the free atom constitutes an irreducible representation of the symmetry group of the sphere, with definite total angular momentum J and definite parity. The state is $(2J + 1)$ -fold degenerate. Now we introduce the atom into a field having the symmetry of one of the 58 magnetic classes, and try to find the resulting term splitting.*

The symmetry group G of a magnetic class can be divided into two parts (cf. reference 3). The first part consists of all the "rotations" in the group G and does not include transformations involving the time inversion. These "rotations" form a subgroup H of index 2 in the group G , i.e., H contains half the elements of G . The symmetry elements of G which are not contained in H are products of "rotations" and the time inversion.

To find the term splitting we proceed as follows. First we consider the term splitting which would occur if H were the symmetry group of the perturbing field. This splitting is found in the usual fashion by expanding the irreducible representation corresponding to the free atom state in irreducible representations of H . In doing this, it is necessary to count nonequivalent complex-conjugate irreducible representations as belonging to different components in the split term. The resulting splitting will be more complete than the actual splitting since the symmetry of H is lower than the actual symmetry of the perturbed atom. Actually the presence in G of symmetry elements which are not contained in H can lead to indistinguishability of components corresponding to different irreducible representations of H . Consequently to find the actual splitting of atomic terms under the influence of a perturbation with the symmetry G we must establish how the irreducible representations of H change under the action on the basis of the representation of those symmetry elements in G which are not in H . The initial and the resultant representations are to be counted as belonging to the same component.

It is obviously sufficient to take only those ele-

*We are interested only in the number and degeneracy of the components in the splitting of the term. Naturally, the magnitude of the splitting, i.e., the distance between components, cannot be found on the basis of symmetry alone.

TABLE I. Tabulation of the 35 magnetic classes G whose "rotation" subgroup H has only real irreducible representations

G	H	G	H	G	H
$\bar{1}$	1	$\bar{4}$	2	$\bar{3}m$	3m
$\bar{2}$	1	$\bar{4}2$	222	$\bar{6}2m$	3m
\bar{m}	1	$\bar{4}/m$	2/m	$\bar{6}2$	32
$\bar{2}/m$	2	$\bar{4}mm$	2mm	$\bar{6}2m$	32
$\bar{2}/m$	m	$\bar{4}/mmm$	42	$\bar{6}mm$	3m
$\bar{2}/m$	$\bar{1}$	$\bar{4}/mmm$	4mm	$\bar{6}/mmm$	$\bar{6}2m$
222	2	$\bar{4}/mmm$	mmm	$\bar{6}/mmm$	$\bar{3}m$
2mm	2	$\bar{4}/mm.m$	$\bar{4}2m$	$\bar{6}/mmm$	62
2mm	m	$\bar{4}$	2	$\bar{6}/mmm$	6mm
mmm	222	$\bar{4}2m$	222	$\bar{m}3m$	43
mmm	2mm	$\bar{4}2m$	2mm	$\bar{m}3m$	$\bar{4}3m$
mmm	2/m	$\bar{3}m$	32		

ments which when adjoined to H generate the whole group G.

Since the subgroup H has index 2, it is sufficient to adjoin to it any element of G-H in order to get G. We denote this element by RB, where R is the time inversion and B is some "rotation."

4. Let us consider any irreducible representation of the group, with the basis $\psi_1(x), \psi_2(x), \dots, \psi_n(x)$, where x is the set of arguments of the wave functions. The action of RB on the basis functions can be divided into the action of the "rotation" B and the action of the time inversion. In the present paper we limit ourselves to the case of integral J. In this case the results of including symmetry under time inversion are the same as when the spin is omitted entirely.² Thus we may assume that the wave functions satisfy the Schrödinger equation and are consequently transformed into their complex conjugates by the time inversion.

The 58 magnetic classes which do not reduce to the 32 crystallographic classes can be divided into two categories. Those magnetic classes whose groups have only real irreducible representations, (where by a real representation we mean one whose characters are real numbers), belong to the first category, while the remaining magnetic classes belong to the second.

Let us consider the change in the irreducible representations of the first category of groups when the element B acts on the basis. We choose a basis consisting of real functions. In this case the "rotation" B transforms the old basis into a new one which again consists of real functions.

Then the subsequent action on the basis by the element R produces no change. Thus the action of RB on the basis reduces to that of the "rotation" B alone. The splitting of the term will be the same as it would be if the time inversion R were replaced by the unit element E in the symmetry group of the perturbing field. Thus for those magnetic classes for which the representations are real, we can obtain the splitting of the atomic term by the standard procedure, as in reference 1, by choosing as the symmetry group the crystallographic class G' which is obtained from the magnetic class G by replacing R by E.

By using the table of characters of irreducible representations of the groups of the crystallographic classes (cf. for example reference 5), it is easy to find all the magnetic classes belonging to the first category. There are 35 such classes (Table I).

We now go over to those magnetic classes for which the subgroup H has complex representations. For these magnetic classes, the action of elements RB on the basis of the irreducible representations of H does not reduce to the action of a "rotation" alone.

Under the action of B, the basis ψ_i changes to $\psi_i' = B_{ik}\psi_k$, and the representation $T(h)$, where h is an element of H, changes into $BT(h)B^{-1}$. The additional action of R on the basis changes the basis functions and the representations to their complex conjugates. The net result is that RB changes the representation $T(h)$ to $(BT(h)B^{-1})^*$. We must now demand

TABLE II. Characters of irreducible representations of the group 4

Irreducible representations	Group elements			
	E	L_4	L_2	L_4^{-1}
A	1	1	1	1
B	1	-1	1	-1
E_1	1	i	-1	$-i$
E_2	1	$-i$	-1	i

that the representations $T(h)$ and $(BT(h)B^{-1})^*$ belong to the same component in the split term. We note that $BT(h)B^{-1} = T(BhB^{-1})$. The rotations B and h form the group G' , which is obtained from G if the element RB is replaced by B . The group H will be a subgroup of index 2 in G as well as in G' . We know that every subgroup of index 2 is a normal divisor (invariant subgroup). Therefore the element BhB^{-1} belongs to the subgroup H . Consequently the change of the representation under transformations of the type RB is found by using the table of irreducible representations. Actually the matter is further simplified by the fact that the irreducible representations are given by their characters.

We shall first apply these considerations to two examples. Suppose the atom is in a field of symmetry* $4/\underline{m}$: $E, L_4, L_2, L_4^{-1}, R\sigma_h, RS_4, Ri, RS_4^{-1}$. Here the subgroup H will be the group $4(C_4)$: E, L_4, L_2, L_4^{-1} . The group 4 has the irreducible representations A, B, E_1, E_2 (cf. Table II). It is most convenient to choose Ri as the element RB . The elements BhB^{-1} are $ih^{-1} = h$, i.e., the matrix $T(h)$ and consequently the character $\chi(h)$ are not changed by the "rotation" i . The time inversion changes $\chi(h)$ to $\chi^*(h)$. This means that the irreducible representations A and B are not changed, while the irreducible representations E_1 and E_2 are transformed into one another. Consequently the representations E_1 and E_2 are indistinguishable in our problem. Thus in this example the splitting occurs as for a perturbation with symmetry 4, but the complex conjugate irreducible representations E_1 and E_2 belong to the same doubly degenerate subterm.

Let us treat another example. Suppose that the atom is in a field with the symmetry $4\underline{mm}$: $E, L_4, L_2, L_4^{-1}, 4R\sigma_v$. The subgroup H is again

*We use the "international" notation for designating the symmetry classes, where the dash below a symbol means that instead of the underlined element we should take its product with the time inversion.

TABLE III. Summary of the 12 magnetic classes for which inclusion of magnetic symmetry leads to no additional degeneracy

G	H
$\underline{42}$	4
$\underline{4mm}$	4
$\underline{4/mmm}$	4/m
$\underline{\bar{4}2m}$	$\bar{4}$
$\underline{32}$	3
$\underline{3m}$	3
$\underline{\bar{3}m}$	$\bar{3}$
$\underline{\bar{6}2m}$	$\bar{6}$
$\underline{62}$	6
$\underline{6mm}$	6
$\underline{6/mmm}$	6/m
$\underline{\bar{4}3m}$	23

the group 4. As the element RB it is convenient to choose $R\sigma_x$. The elements BhB^{-1} will be L_4^{-1} for L_4, L_4 for L_4^{-1} , and L_2 itself for L_2 . From this we see that the irreducible representations A and B are transformed into themselves by the "rotation" σ_x , while the complex conjugate representations E_1 and E_2 transform into one another. Application of R again does not change A and B , while the complex conjugate representations E_1 and E_2 once again change places. Thus as a result of applying $R\sigma_x$ each irreducible representation of 4 goes over into itself. Consequently the splitting when the symmetry of the perturbation is $\underline{4mm}$ will be the same as when the symmetry is 4, and the complex conjugate irreducible representations must be counted as belonging to two different nondegenerate subterms.

All 23 magnetic classes for which the "rotation" subgroup H has complex irreducible representations are treated analogously to the examples presented above. One finds the result that the splitting is the same as when one includes only the symmetries in the subgroup H instead of the whole symmetry of the magnetic class, with the one important proviso that in 12 cases the complex conjugate irreducible representations of the subgroup H correspond to different nondegenerate subterms (Table III), while in the other 11 cases the complex conjugate irreducible representations of the subgroup H must be counted as belonging to the same doubly-degenerate component in the splitting of the term of the unperturbed atom (Table IV).

TABLE IV. Summary of the 11 magnetic classes for which inclusion of magnetic symmetry leads to additional degeneracy

G	H
$4/m$	4
$\overline{4/m}$	$\overline{4}$
$\overline{3}$	3
$\overline{6}$	3
6	3
$\overline{6/m}$	$3/m$
$\overline{6/m}$	6
$\overline{6/m}$	$\overline{3}$
$\overline{m3}$	23
$\overline{43}$	23
$\overline{m3m}$	$m3$

From the group-theoretical point of view these cases differ in that in the first case the classes of conjugate elements of the group H do not coincide with the classes of conjugate elements of H when it is regarded as a subgroup of G , whereas in the second case the classes of conjugate elements are the same whether H is regarded as a subgroup of G or as a group by itself.

5. Let us discuss the results and explain the effect of inclusion of magnetic symmetry on the splitting of terms compared to the splitting when only the crystallographic symmetry is taken into account.

Disregard of the magnetic symmetry, i.e., omission of elements like RA , means that instead of the actual symmetry G of the perturbed atom we are taking the subgroup H of G which contains only "rotations." However, when this is done it is not assumed that there is no magnetic interaction.

In the case of magnetic symmetry, when the magnetic class coincides with one of the 32 crystallographic classes, elements like RA do not occur in the symmetry group, and the magnetic symmetry of the crystal field coincides with the crystallographic symmetry. Because of the presence of the magnetic interaction, the crystal field is not invariant with respect to R , so that the nonequivalent complex conjugate irreducible representations correspond to different components in the splitting of the term.

The other case of magnetic symmetry is that in which the magnetic class contains elements of the type RA , while the subgroup H containing

all the "rotations" has only real irreducible representations (Table I). In this case the consideration of the magnetic symmetry, i.e., the inclusion of elements of the type RA , is essential. The removal of the degeneracy will in general be less complete than when only the crystallographic symmetry (i.e., the subgroup H) is considered. Despite the presence of the magnetic interaction, the removal of the degeneracy may be incomplete.

In the third case (Table III), taking account of the magnetic symmetry does not lead to new results. The presence of magnetic interaction results in the perturbed atom being nonsymmetric with respect to R .

In the fourth case (Table IV), the magnetic symmetry elements make those components in the splitting indistinguishable which belong to complex conjugate irreducible representations of the crystallographic symmetry group.

6. The treatment given above refers not only to the splitting of atomic terms in a magnetic crystal, but can also be applied without any restriction to the splitting of atomic terms in a nonmagnetic crystal which is in an external magnetic field. In this case the symmetry of the perturbed atom will contain the symmetry elements which are common to the crystal symmetry and to the symmetry of the external magnetic field for the given orientation of the crystal in the field; by the symmetry of the crystal we here mean its crystallographic class multiplied by R . If the orientation of the crystal in the field is arbitrary, the removal of the degeneracy will be complete, since there is no symmetry. But for certain positions of the crystal relative to the field it may happen that the degeneracy is not completely removed, in which case the consideration of magnetic symmetry is essential.

We also note that an atom in a uniform magnetic field has the symmetry $\infty/m\overline{m}$, and belongs to case 3 (Table III), for which consideration of the magnetic symmetry does not change the term splitting. This is in accord with the fact that the Zeeman effect is obtained correctly from symmetry considerations without taking magnetic symmetry into account.

In conclusion I express my thanks to Academician L. D. Landau and Prof. B. T. Geilikman for discussions.

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EFFECT OF THERMOELECTRIC FORCES ON THE SKIN EFFECT IN A METAL

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The surface impedance of a metal is calculated with thermoelectric forces taken into account.

1. In the calculation of the surface resistance (impedance) of metals, one usually starts with Ohm's law,

$$j_i = \sigma_{ik} E_k,$$

where σ_{ik} is the conductivity tensor, and \mathbf{E} and \mathbf{J} are the vector electric field intensity and current density.* One thereby neglects the effect of heat waves that are produced in the metal by passage of an electromagnetic wave through it. As will be evident later, this is correct only in isotropic metals in the absence of a magnetic field, and in anisotropic metals when the surface of the metal coincides with a principal plane of the resistivity tensor.

The complete system of equations describing the propagation of waves in a metal, with heat flow taken into account, has the form

$$\begin{aligned} \text{curl} \mathbf{H} &= \frac{4\pi}{c} \mathbf{j}; \text{curl} \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{H}}{\partial t}; \quad C \frac{\partial \Theta}{\partial t} + \text{div} \mathbf{q} = 0; \\ E_i &= \sigma_{ik} j_k + \alpha_{ik} \partial \Theta / \partial x_k; \quad q_i = T \alpha_{ik} j_k - \kappa_{ik} \partial \Theta / \partial x_k. \end{aligned} \quad (1)$$

Here Θ is the high-frequency addition to the mean temperature T of the specimen; C is the heat capacity of unit volume of the metal; \mathbf{q} is the heat current; ρ_{ik} is the resistivity tensor; κ_{ik} is the heat conductivity tensor; and

*We are interested here in the range of frequencies and temperatures in which there is a normal skin effect.

α_{ik} is the tensor of thermoelectric coefficients.

The tensor α_{ik} , in general, is not symmetric. However, all metals possess lattice symmetry that excludes an antisymmetric part of the tensor α_{ik} . Therefore we shall hereafter suppose, in the absence of a magnetic field, that $\alpha_{ik} = \alpha_{ki}$.

Besides the usual boundary conditions of continuity of the tangential components of the vectors \mathbf{E} and \mathbf{H} , we must add to the system of equations (1) boundary conditions for the temperature. We shall consider two limiting cases:

(a) Heat current equal to zero at the surface:

$$\mathbf{q} \cdot \mathbf{n} = 0 \quad (2a)$$

(\mathbf{n} = unit vector normal to the surface).

(b) Surface temperature maintained constant and equal to T :

$$\Theta = 0. \quad (2b)$$

2. We consider normal incidence of a plane monochromatic electromagnetic wave, of frequency ω , on the surface of a uniaxial metal, whose principal axis (1 in the figure) makes an angle φ with the normal to the surface of the metal; we choose for the z axis the direction of the normal. Then all quantities (\mathbf{E} , \mathbf{H} , Θ) depend on the coordinate z alone. With the x and y axes chosen as shown in the figure, it is easy to show that $\rho_{xy} = \rho_{yx} = \rho_{xz} = 0$ and $\alpha_{xy} = \alpha_{yx} = \alpha_{zx} = 0$. It follows furthermore from Maxwell's equations, in this case, that $j_z = 0$