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Generalized Kittel–Van Vleck Relation between g and g': Validity for Negative g Factors

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It is pointed out that a generalized exact relationship exists between the spectroscopic splitting factor g and the magnetomechanical ratio g' for paramagnetic centers: $g'=g/(g-\rho)$ with $\rho=\langle S_z\rangle/S_z'$. Here S' is the fictitious spin in the spin Hamiltonian and $\langle S_z\rangle$ is the expectation value of the real spin in the state labeled by S_z'; the z axis is defined by the direction of magnetic field. Several classes of magnetic systems are considered, where for each system ρ is constant over a wide range of physical parameters such as cubic crystal field and spin-orbit coupling, expressing an underlying symmetry of the magnetic ion in its environment. It is shown that the sole criterion for validity of the Kittel–Van Vleck relation $g'=g/(g-1)$ is that $\langle S_z\rangle=S_z'$ and that this may occur even when the admixed orbital angular momentum is very large so that the departure of g from 2 is very large. The generalized relation between g and g' is also applied to cases where g is negative while g' is positive. The extension of the relation between g and g' to cases of interacting magnetic centers is discussed.

I. INTRODUCTION

MEASUREMENTS on paramagnetic crystals in an external magnetic field lead to the introduction of two quantities related to the magnetic moment. These are the magnetomechanical ratio g' and the spectroscopic splitting factor g (the g factor). The magnetomechanical ratio of an ion is the ratio of its magnetic moment measured in units of the Bohr magneton μ_B to its angular momentum in units of $\hbar$. g' is usually measured by an Einstein–de Haas experiment in which the magnetic field that is used to produce the magnetization is switched off (or modulated at a low frequency) and the change in the electronic angular momentum connected with the change in magnetization is observed as an angular momentum transferred to the lattice of the specimen. The relaxation of the electronic moment is accomplished by processes internal to the crystal (i.e., nonradiative). The g factor, on the other hand, measures the energy splitting of a degenerate state by a magnetic field and is defined (for a doubly degenerate state) by $\Delta E=g\mu_BH$.

Although in free ions the quantities g and g' are identical, in a solid the crystalline field may act on the orbital coordinates and alter the simple scheme of the free ion. The removal of some (or all) of the orbital degeneracy causes a torque to act on a precessing moment, and as a result g and g' represent different physical quantities which may indeed have different signs. Thus g' gives the sign and magnitude of the magnetic moment due to the microscopic charges precessing around the direction of the resultant angular momentum, while g gives the sign and magnitude of the precession of the magnetic moment around the direction of the external magnetic field. g is different from g' because the torque equation $\dot{\mathbf{J}}=\mathbf{M}\times\mathbf{H}$ does not hold in a crystalline environment. As pointed out by Kittel,[1] there is a strong analogy between the g factor and the effective mass of an electron in a crystal lattice; as the lattice exerts a force on an accelerating electron, so it exerts a torque on a precessing moment and it is this torque that results in $g\neq g'$. This difference has been extensively discussed by Kittel[1] and Van Vleck[2] who have given the relation

$$g'=g/(g-1) \tag{1}$$

between g and g' when both are close to the free-spin value $g=2$. More explicitly, they assumed that the state in question had only a small admixture of orbital angular momentum so that its magnetization and angular momentum were predominantly due to spin (such as the ground states of Fe^{3+} or Ni^{2+} in cubic crystal fields).[3] Under these circumstances the signs of g and g' would be the same and be that of a free-electron spin.

With the introduction of the spin Hamiltonian for the description of paramagnetic states, it was generally assumed that the sign of the g value was arbitrary and could be changed by reversing the sign of the z component of fictitious spin S_z'. It was pointed out by Pryce,[4] however, that not only a magnitude (as implied by the definition given above) but, under certain circumstances of symmetry, a sign as well, can be ascribed to the g value as will be made clear later. The physical meaning of this sign is that it tells the sense of precession of the magnetic moment in the external field, a negative g

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[1] C. Kittel, Phys. Rev. **76**, 743 (1949).

[2] J. H. Van Vleck, Phys. Rev. **78**, 266 (1950).

[3] Magnetomechanical effects for paramagnetic systems have also been treated by C. J. Gorter and B. Kahn, Physica **7**, 753 (1940).

[4] M. H. L. Pryce, Phys. Rev. Letters **3**, 375 (1959).

factor meaning that the moment precesses in the direction opposite to that of a free-electron spin.

Recently, we noticed that for Ce^{3+} in yttrium ethyl sulphate, the g factor was negative, while g' was expected to be very close to the Landé factor g_J and hence be positive. This and other cases with g and g' of opposite signs will be discussed below. The difference in sign seemed paradoxical to us and we looked for some relation between g and g' which would not be restricted by perturbation theory as is the Kittel–Van Vleck relation.

We have found a relationship [Eq. (22), below] between g and g' that is valid under far less restrictive assumptions than implied by the original derivation of Eq. (1), i.e., it is not necessary that the admixed orbital angular momentum be small. The criterion for validity of Eq. (1) is that the fictitious spin be equal to the expectation value of the real spin, independent of how large the orbital angular momentum might be. The modification of Eq. (1) for the case where g and g' are opposite in sign follows from the generalized relation derived below.

In Sec. II, we consider the spin-Hamiltonian definitions of g and g' and their relative signs following, in the latter case, the work of Pryce.[4] In Sec. III, we discuss the Kittel-Van Vleck relation and its generalization with several illustrations. The discussion of g and g' centers around an isolated set of magnetically degenerate states of noninteracting, fixed paramagnetic centers. We have chosen to fix our attention upon such relatively simple systems in spite of the fact that in the past most of the experimental situations to which the relation between g and g' has been applied dealt with ferromagnetic substances. This course has been adopted as the basic physical principles involved in the relation between g and g' are best illustrated by these simplest paramagnetic systems. In Sec. IV, we briefly consider the effect of exchange interactions in insulators and metals.

II. DEFINITION OF g AND g' IN THE SPIN HAMILTONIAN

A. Spin Hamiltonian

The spin Hamiltonian provides a convenient framework for the representation of the matrix elements of operators in a manifold consisting of a few low-lying states of the system.[5] In particular, we can represent the angular momentum **J** and the magnetic moment **M** in this way, and this proves useful in the definition of the quantities g and g'.

Let us suppose that we are interested in matrix elements within a manifold of n states $|\psi_1\rangle, \cdots, |\psi_n\rangle$. The matrices of any operator A will then, within these states, be n-dimensional, with n^2 constants. The spin-Hamiltonian operator equivalent of A is obtained by identifying each of the states $|\psi_1\rangle, \cdots, |\psi_n\rangle$ with one of the eigenstates of the z component S_z' of a fictitious spin $S'=\frac{1}{2}(n-1)$. (The prime on the fictitious spin operators will be used to distinguish them from the true spin.) The n^2 constants can then be represented by the coefficients of the operators $\mathbf{1}$ (identity operator), S_x', S_y', S_z', $S_x'S_y'$, $\cdots$ (all products of degree $<n$). The advantage of this specification is that all operators are represented by sums or products of angular momentum operators, and the well-developed algebra of angular momentum can be used. For each operator in real space, then, there exists a corresponding operator equivalent in fictitious spin space, and the construction of the spin Hamiltonian involves the determination of these operator equivalents.

It should be emphasized that the coordinate axes in fictitious spin space are in general not related to those in real space, so that we might write S_ξ', S_η', S_ζ' in place of S_x', S_y', S_z'. We use the present notation since, as discussed in the following, the fictitious spin space is chosen to make it correspond as closely as possible to real space. The distinction should be kept in mind, however, as it is important in treating the transformation properties of quantities such as the g matrix, which has one index referring to real space and another to fictitious spin space.

In the following, we will restrict our discussion to the case $n=2$, i.e., to systems for which the lowest energy level is twofold degenerate. The case of higher degeneracy will be touched on briefly, for special cases, in a later section. If the ground state is twofold degenerate, the spin Hamiltonian can be constructed from the spin operators for $S'=\frac{1}{2}$. The matrices of all operators within the ground manifold will be 2×2 matrices, and it is well known that any such matrix can be represented as a linear combination of the unit matrix and S_x', S_y', S_z'. We suppose then, that $|a\rangle$ and $|b\rangle$ are the doubly degenerate ground levels in real space. To construct the spin Hamiltonian, we identify the states $|\pm\frac{1}{2})$ in a fictitious spin-$\frac{1}{2}$ space with $|a\rangle$ and $|b\rangle$. States in the fictitious space will be denoted by round brackets: $|\pm\frac{1}{2})$; true states will be denoted by angular brackets: $|a\rangle$, so that $|a\rangle \leftrightarrow |+\frac{1}{2})$ and $|b\rangle \leftrightarrow |-\frac{1}{2})$. Any operator A will have four matrix elements within this pair of levels, namely, $\langle a|A|a\rangle$, $\langle a|A|b\rangle$, $\langle b|A|a\rangle$, $\langle b|A|b\rangle$. The operator equivalent of A in the fictitious spin space A_{eq} is chosen so that the matrix elements of A within the states $|a\rangle$ and $|b\rangle$ are equal to those of A_{eq} within $|\pm\frac{1}{2})$. If we use the standard representation for the spin-$\frac{1}{2}$ matrices,

$$S_x'=\frac{1}{2}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad S_y'=\frac{1}{2}\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix},\quad S_z'=\frac{1}{2}\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix},$$

then it is apparent that

$$A_{\mathrm{eq}}+\alpha_0\mathbf{1}+\boldsymbol{\alpha}\cdot\mathbf{S}'=\alpha_0\mathbf{1}+\alpha_xS_x'+\alpha_yS_y'+\alpha_zS_z', \qquad (2)$$

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[5] See, for example, K. W. H. Stevens, in *Magnetism*, edited by H. Suhl and G. T. Rado (Academic Press Inc., New York, 1963); and C. Herring *ibid.*, Vol. IIb, p. 20 ff.

where the constants α are given in terms of the matrix elements of A by

$$\begin{aligned} \alpha_0 &= \tfrac{1}{2}(\langle a|A|a\rangle + \langle b|A|b\rangle)\,, \\ \alpha_x &= \langle a|A|b\rangle + \langle b|A|a\rangle\,, \\ \alpha_y &= i(\langle a|A|b\rangle - \langle b|A|a\rangle)\,, \\ \alpha_z &= \langle a|A|a\rangle - \langle b|A|b\rangle\,. \end{aligned} \qquad (3)$$

The above choice of the spin matrices implies that we use a right-handed coordinate system in spin space, but the constants are to a certain degree still arbitrary. One might choose to identify $|-\frac{1}{2}\rangle$ with $|a\rangle$ or, indeed, with any linear combination of $|a\rangle$ and $|b\rangle$, instead of with $|b\rangle$. Such transformations are equivalent to rotations in spin space.

The spectroscopic splitting factor g and the gyromagnetic ratio g' can be defined easily by constructing the operator equivalents for the angular momentum $\mathbf{J}$ and the magnetic moment $\mathbf{M}$. For a doubly degenerate ground manifold we must have

$$\mathbf{M} = -\mu_B(\mathbf{L}+2\mathbf{S}) \rightarrow -g\mu_B\mathbf{S}' \qquad (4)$$

and

$$\mathbf{J} = \mathbf{L}+\mathbf{S} \rightarrow \alpha\hbar\mathbf{S}'\,. \qquad (5)$$

In general, g and α are matrices. It is shown in the Appendix that if the system has orthorhombic (or higher) symmetry, the principal axes of g and α are the same. The gyromagnetic ratio can be obtained in terms of α for these cases by the definition

$$\frac{\langle M_i\rangle/\mu_B}{\langle J_i\rangle/\hbar} = -g_i' = -g_i\langle S'\rangle/\alpha_i\langle S'\rangle = -g_i/\alpha_i\,, \qquad (6)$$

where the index i refers to one of the principal axes, so that

$$\alpha_i = +g_i/g_i'\,, \qquad (7)$$

and

$$\mathbf{J} \rightarrow (\mathbf{g}')^{-1}\mathbf{g}\hbar\mathbf{S}'\,. \qquad (8)$$

From this discussion we see that the question of a relation between g and g' reduces to the relation between the constants (reduced matrix elements) in the spin Hamiltonian.

B. Equations of Motion of Equivalent Operators and Sign of g

We have indicated above that the parameters in the spin Hamiltonian are to a certain extent arbitrary. In particular, one might expect the signs of the g factors to be completely arbitrary, since an interchange of $|\pm\frac{1}{2}\rangle$ causes a change in sign of g_z. Pryce has shown, however, that the product of the signs of the principal g factors is constant, and that this sign has the physical significance of the direction of precession of the magnetic moment in the magnetic field.

As the equation of motion for $\mathbf{M}$ will be expressed in terms of operator equivalents, we first wish to make some remarks about how equations of motion involving operators in real space are carried over into equations of motion in terms of the operator equivalents. Construction of equivalent operators for a spin Hamiltonian is done by requiring that the matrix elements *within the ground manifold* in real space of the real operators be equal to the matrix elements of the operator equivalents in the fictitious spin states. This implies that the operator equivalent of the product of two real operators *need not be equal to* the product of the operator equivalents. This is due to the fact that the matrix element of a product may involve states outside the ground manifold,

$$\langle\psi_0|AB|\psi_0'\rangle = \sum_{\varphi}\langle{}^2\psi_0|A|\varphi\rangle\langle\varphi|B|\psi_0'\rangle\,, \qquad (9)$$

where ψ_0, ψ_0' are states of the ground manifold, and φ runs over *all* states.

If both A and B have matrix elements connecting the ground manifold to the same excited state, this product will involve matrix elements whose definition is not required for the definition of the operator equivalent in fictitious spin space. If either A or B has no matrix elements connecting the ground manifold to excited states, the operator equivalent of the product will be equal to the product of the operator equivalents. The *full* Hamiltonian $\mathcal{H}$, including spin-orbit coupling, crystal-field interactions, and the Zeeman interaction clearly has this property. In practice, of course, the Hamiltonian is not diagonalized exactly, but only to some order in perturbation theory, but to this order the equations of motion can be taken over to the fictitious spin space

$$i\hbar\dot{A} = [A,\mathcal{H}] \rightarrow i\hbar\dot{A}_{\mathrm{eq}} = [A_{\mathrm{eq}},\mathcal{H}_{\mathrm{eq}}]\,. \qquad (10)$$

Hence, following Pryce,[4] we may write for the equation of motion

$$i\hbar\dot{\mathbf{M}}_{\mathrm{eq}} = [\mathbf{M}_{\mathrm{eq}},\mathcal{H}_{\mathrm{eq}}] = [\mathbf{M}_{\mathrm{eq}},\ -\mathbf{M}_{\mathrm{eq}}\cdot\mathbf{H}]\,. \qquad (11)$$

Since $M_{\mathrm{eq}}{}^{\alpha} = -g_\alpha\mu_B S_\alpha'$, we find, after using the commutation relations for the S_α', that

$$\dot{M}_{\mathrm{eq}}{}^{x} = \frac{\mu_B}{\hbar}\left(\frac{g_xg_y}{g_z}H_yM_{\mathrm{eq}}{}^{z} - \frac{g_xg_z}{g_y}H_zM_{\mathrm{eq}}{}^{y}\right),\ \text{etc.} \qquad (12)$$

The magnitude of each g has physical significance, as does the sign of the product $g_xg_yg_z = \det g$, which determines the sense of the precession of $\mathbf{M}$ around $\mathbf{H}$. If the system has axial symmetry, it is reasonable (but not necessary) to choose $g_x = g_y = g_\perp$, so that the sign of $g_z = g_{||}$ as well as its magnitude is specified. As Pryce points out, interchanging $|a\rangle$ and $|b\rangle$ changes the sign of g_y and g_z, but not of g_x. This leads, in a system with axial symmetry, to $g_y = -g_x$. While this is permissible it is unappealing, since we prefer that the fictitious spin space reflect the symmetries of physical space.

The conclusion given here and by Pryce is in contradiction to statements made by Pearson, Hermann, Wickersheim, and Buchanan,[6] who state that it is possible to determine the sign of the g factor along symmetry axes. This is a matter of convention, and the only physically measurable sign is that of the product of the three principal g factors.

C. Opposite Signs of g and g' in Cubic Symmetry

We may illustrate much of the preceding discussion with some simple examples. Consider first the case of a rare-earth ion with a single hole in the f shell in a cubic field. Spin-orbit coupling (assumed large compared to the cubic field) gives $J=\frac{5}{2}$ and $J=\frac{7}{2}$, with the latter lower. The $J=\frac{7}{2}$ level is then split by the cubic field into a Γ_6 doublet, a Γ_7 doublet, and a Γ_8 quartet. Before writing down the wave functions for these levels, we may show that $g'=+g_J$, the Landé factor, in each case. This follows because these levels are made up entirely of $J=\frac{7}{2}$ states. The matrix elements of the vector operator $\mathbf{M}=-\mu_B(\mathbf{L}+2\mathbf{S})$ are, within such levels, proportional to those of $\mathbf{J}$, and in particular $M\rightarrow -\mu_B g_J \mathbf{J}$, where

$$g_J=1+[J(J+1)-L(L+1)+S(S+1)]/[2J(J+1)].$$

Hence, from the above definition of g',

$$g'=+g_J.$$

We emphasize that this relation holds as long as the ground-state levels are made up of states for which J is a good quantum number. Note that it is possible in principle for g_J to take either a positive or a negative sign. For example for $S=\frac{5}{2}$, $L=3$, $J=\frac{1}{2}$ one has $g_J=-\frac{2}{3}$. However, for the Hund's rule ground states of the rare earths g_J is always positive.

The wave functions for the Γ_6 and Γ_7 levels are given by[7]

$$|\Gamma_6\alpha\rangle=\surd(5/12)|\tfrac{7}{2}-\tfrac{7}{2}\rangle+\surd(7/12)|\tfrac{7}{2}\tfrac{1}{2}\rangle, \tag{13a}$$

$$|\Gamma_6\beta\rangle=+\surd(5/12)|\tfrac{7}{2}\tfrac{7}{2}\rangle+\surd(7/12)|\tfrac{7}{2}-\tfrac{1}{2}\rangle, \tag{13b}$$

$$|\Gamma_7\alpha\rangle=\tfrac{1}{2}\sqrt{3}|\tfrac{7}{2}\tfrac{5}{2}\rangle-\tfrac{1}{2}|\tfrac{7}{2}-\tfrac{3}{2}\rangle, \tag{14a}$$

$$|\Gamma_7\beta\rangle=\tfrac{1}{2}\sqrt{3}|\tfrac{7}{2}-\tfrac{5}{2}\rangle-\tfrac{1}{2}|\tfrac{7}{2}\tfrac{3}{2}\rangle. \tag{14b}$$

Consider the Γ_7 doublet first. We make the identification $|\Gamma_7\alpha\rangle\rightarrow|+\frac{1}{2})$ and $|\Gamma_7\beta\rangle\rightarrow|-\frac{1}{2})$. Then

$$\begin{aligned}\langle\Gamma_7\alpha|M^z|\Gamma_7\alpha\rangle&=-g_z\mu_B(\tfrac{1}{2}|S_z'|\tfrac{1}{2})=-\tfrac{1}{2}g_z\mu_B\\&=-g_J\mu_B\langle\Gamma_7\alpha|J^z|\Gamma_7\alpha\rangle\\&=-g_J\mu_B(\tfrac{3}{4}\times\tfrac{5}{2}-\tfrac{1}{4}\times\tfrac{3}{2})=-\tfrac{3}{2}g_J\mu_B,\end{aligned} \tag{15}$$

so that $g_z=3g_J$. This identification leads to the same values of g_x and g_y, as cubic symmetry leads us to expect. We may note that the operator $S_+'\equiv S_x'+iS_y'$ connects the state $|-\frac{1}{2})$ to $|+\frac{1}{2})$. For this doublet, the spin Hamiltonian gives $g'=+g_J$ and $g=3g_J$. Let us now consider the Γ_6 doublet. If we identify $|\Gamma_6\alpha\rangle\rightarrow|+\frac{1}{2})$ and $|\Gamma_6\beta\rangle\rightarrow|-\frac{1}{2})$, we have

$$\begin{aligned}\langle\Gamma_6\alpha|M^z|\Gamma_6\alpha\rangle&=-g_z\mu_B(\tfrac{1}{2}|S_z'|\tfrac{1}{2})=-\tfrac{1}{2}g_z\mu_B\\&=-g_J\mu_B\langle\Gamma_6\alpha|J_z|\Gamma_6\alpha\rangle\\&=-g_J\mu_B\{(5/12)\times(-\tfrac{7}{2})+(7/12)\times\tfrac{1}{2}\}\\&=+(7/6)g_J\mu_B,\end{aligned} \tag{16}$$

so that $g_z=-(7/3)g_J$; i.e., the g factor is negative. We may be tempted to change the identification of the levels, so that $|\alpha\rangle\rightarrow|-\frac{1}{2})$ and $|\beta\rangle\rightarrow|+\frac{1}{2})$. This would certainly change the sign of g, but we would then find that, since

$$\langle\Gamma_6\alpha|J_+|\Gamma_6\beta\rangle\neq 0$$

and

$$\langle\Gamma_6\beta|J_+|\Gamma_6\alpha\rangle=0,$$

we would have $J_+\rightarrow \text{const}\times S_-'$ and $J_-\rightarrow \text{const}\times S_+'$. The spin Hamiltonian would then no longer display the cubic symmetry explicitly since then we would have, as in the axial case discussed above, $g_x=-g_y=g_z$. We are left with the choice $g_x=g_y=g_z=-(7/3)g_J$; $g'=+g_J$. We conclude that, in the presence of a magnetic field, the magnetization for the Γ_6 levels precesses in the opposite sense from the magnetization in the Γ_7 levels. *In each case*, however, the gyromagnetic ratio g' is the same, namely, $+g_J$. These examples illustrate the varieties of behavior possible for the g and g' factors, even in cubic symmetry, and for doublets arising from the same multiplet.

III. GENERALIZED KITTEL-VAN VLECK RELATION

A. Criterion for Validity of the Kittel-Van Vleck Relation and Its Generalization

We now reexamine the well-known Kittel-Van Vleck relation between g and g'. We wish to consider the essential approximations made as well as ask how the Kittel-Van Vleck relation is to be modified and generalized, particularly for negative g values.

Let us consider a manifold of n states which are degenerate in the absence of a magnetic field and whose splitting in a magnetic field (the direction of which defines the z axis) is described by

$$W=g\beta HS_z'=\beta H[\langle L_z\rangle+2\langle S_z\rangle]_{S_z'}, \tag{17}$$

where n is related to the fictitious spin S_z' by $2S_z'+1=n$. The subscript S_z' denotes that the averages are to be taken in the state associated with S_z'. In the following, all averages are to be understood in this way.

From Eq. (17), we have

$$g=(\langle L_z\rangle+2\langle S_z\rangle)/S_z', \tag{18}$$

where g is the spectroscopic splitting factor. The gyromagnetic factor for this manifold of states will be given by Eq. (6) above, i.e.,

$$g'=\frac{2mc}{e}\frac{\langle M_z\rangle}{\langle J_z\rangle}=\frac{\langle L_z\rangle+2\langle S_z\rangle}{\langle L_z\rangle+\langle S_z\rangle}. \tag{19}$$

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[6] J. J. Pearson, G. F. Hermann, K. A. Wickersheim, and R. A. Buchanan, Phys. Rev. **159**, 251 (1967), Appendix D.

[7] J. S. Griffith, *The Theory of Transition Metal Ions* (Cambridge University Press, Cambridge, 1961).

If now we make the assumption that

$$S_z' = \langle S_z \rangle, \tag{20}$$

then from (18)–(20) there follows the Kittel-Van Vleck relation given in Eq. (1):

$$g' = g/(g-1).$$

Note that the essential assumption is that $S_z' = \langle S_z \rangle$ with no reference whatsoever to how large $\langle L_z \rangle$ might be. Furthermore, in addition to the fact that g may be very large, it may also be either positive or negative. We stress this point because in the original derivations,[1,2] a perturbation theory approach was used which implied $\langle L_z \rangle$ was small, from which it followed that $S_z' = \langle S_z \rangle$. For example, an orbital singlet state was considered in which the angular momentum was quenched and the g shift arose from the admixture of orbital angular momentum from excited states by application of spin-orbit coupling, $\lambda \mathbf{L}\cdot\mathbf{S}$ only to first order, i.e., from a term of the type

$$\langle 0|\mathbf{H}\cdot\mathbf{L}|n\rangle\langle n|\lambda\mathbf{L}\cdot\mathbf{S}|0\rangle/\Delta,$$

where $|0\rangle$ is the ground state and $|n\rangle$ refers to excited states. Since $\mathbf{H}\cdot\mathbf{L}$ does not connect different spin components, using λ to first order in this way preserves the spin state while admixing orbital angular momentum so that $\langle S_z \rangle = S_z'$. In contrast, if we consider a second-order g shift to a power λ^2, then the initial spin state $|S_z\rangle$ may be mixed with $|(S_z+1)\rangle$ and $|(S_z-1)\rangle$ so that we can no longer take $S_z' = \langle S_z \rangle$. We stress again, however, that the important criterion for Eq. (1) to hold is that $S_z' = \langle S_z \rangle$ and that this can occur even under circumstances where $\langle \mathbf{L} \rangle$ is quite large, as will be illustrated in a few examples below.

The extension of the Kittel-Van Vleck relation to the most general case with

$$\langle S_z \rangle = \rho S_z', \quad \rho \neq 1 \tag{21}$$

is obvious. Again using (18), (19), and (21), we find that

$$g' = g/(g-\rho). \tag{22a}$$

Note that $\rho = g - \alpha$, where α is defined in Eq. (7). In this sense, Eq. (22a) may be regarded as a general expression connecting g and g', which is valid independent of the sign of g, since a change of sign of g also implies a sign change for ρ.

We prefer, however, to speak of a general relation between g and g' only when ρ is moderately insensitive to a range of values of parameters such as cubic crystal field, spin-orbit coupling, etc., i.e., when ρ reflects some underlying symmetry of the state. Such is the case for an orbital singlet ground state in a cubic crystal field where the spin composition of the ground state is uncontaminated, i.e., when one considers g shifts only to first order in spin-orbit coupling. Another illustration is the Γ_7 doublet of Eq. (14a) and (14b), where $g' = g_J = 8/7$, $g = +24/7$, and $\rho = 3/7$. This value of ρ is constant over a wide range of cubic crystal field strength and spin-orbit coupling as long as J is regarded as a good quantum number and Russel-Saunders coupling holds.

Another interesting example in which symmetry imposes a strong constancy upon ρ is the case of a Co^{2+} ion in octahedral coordination. The free Co^{2+} ion has $S = \frac{3}{2}$ and $L = 3$ with a ^4F ground term. In a cubic field the F term splits into T_1, T_2, and A_2 with the T_1 state lying lowest. A correspondence can be made between the T_1 state and a P state so that the T_1 state can be represented by a fictitious orbital angular momentum $\mathbf{L}' = 1$. The true angular momentum is $\gamma\mathbf{L}$ where matrix elements of $\mathbf{L}$ are to be evaluated for a P state.[7–9] γ has the value $-\frac{3}{2}$ in the weak cubic crystal-field limit and -1 in the strong field limit. When T_1 is combined in this way with $S = \frac{3}{2}$, we get three levels with pseudo $J' = \frac{1}{2}, \frac{3}{2}$, and $\frac{5}{2}$ with the $J' = \frac{1}{2}$ doublet lying lowest. The wave functions for the time reversed states of this doublet are given by the following combinations of product wave functions of S_z and L_z':

$$\psi(+\tfrac{1}{2}) = C_1|\tfrac{3}{2}, -1\rangle + C_2|\tfrac{1}{2}, 0\rangle + C_3|-\tfrac{1}{2}, 1\rangle,$$
$$\psi(-\tfrac{1}{2}) = C_1|-\tfrac{3}{2}, 1\rangle + C_2|-\tfrac{1}{2}, 0\rangle + C_3|+\tfrac{1}{2}, -1\rangle.$$

Now in the case of cubic symmetry, the coefficients C are simply the Clebsch-Gordan coupling coefficients for coupling an angular momentum $J_1 = 1$ to $J_2 = \frac{3}{2}$ to give $J_1 + J_2 = \frac{1}{2}$, i.e., $C_1 = 1/\sqrt{2}$, $C_2 = -1/\sqrt{3}$, and $C_3 = 1/\sqrt{6}$. These coefficients are totally independent of the strength of the cubic crystal field as long as Russel-Saunders coupling holds. Consequently, ρ is a constant and is equal to $\frac{5}{3}$, so that

$$g' = g/(g-\tfrac{5}{3}). \tag{22b}$$

On the other hand, $g = (\frac{2}{3})(5-\gamma)$ and so varies with γ, which in turn depends on the strength of the cubic crystalline field. In contrast, however, if there is also present an *axial* crystal field, then ρ becomes a sensitive function of this axial field.[10] In this case it would not be as meaningful to try to emphasize Eq. (21), since ρ is varying and (21) is no longer an expression of underlying symmetry as in the other cases.

EPR measurements on Co^{2+} in cubic symmetry[11,12] yield g values that fall around the value $g = 13/3$, indicating that γ is close to $-\frac{3}{2}$. Using this g value in Eq. (22b), one finds $g' = 1.625$, which is in fair agreement with some old measurements of Sucksmith on $CoSO_4$ and $CoCl_2$ for which he finds that[13]

$$g'(CoSO_4) = 1.57, \quad g'(CoCl_2) = 1.45.$$

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[8] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[9] J. H. Van Vleck, Physica **26**, 544 (1960).

[10] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951).

[11] W. Low, Phys. Rev. **109**, 256 (1958).

[12] W. Low and R. S. Rubins, in *International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963).

[13] W. Sucksmith, Proc. Roy. Soc. (London) **A133**, 179 (1931).

However, it should be borne in mind, as pointed out by Van Vleck,[9] that the Co^{2+} ion is not in perfect cubic symmetry in these compounds so that one would not expect much better agreement, as ρ is probably not equal to $\frac{5}{3}$. With the recent improved accuracy of g' measurements,[14] it would be very interesting to observe the g' of Co^{2+} in cubic coordination.

B. Opposite Sign of g and g' with Modified Kittel-Van Vleck Relation

The excited $\bar{E}(^2E)$ state of Cr^{3+} in $\mathrm{Al_2O_3}$ offers a very interesting example of a negative g value[15] and a positive g'. This Kramers doublet is represented by the wave functions

$$\bar{E}_+ = |^2E; u_-, +\tfrac{1}{2}\rangle \tag{23a}$$

and

$$\bar{E}_- = |^2E; u_+, -\tfrac{1}{2}\rangle, \tag{23b}$$

where $+\frac{1}{2}$, $-\frac{1}{2}$ refers to the spin quantization, and u_- and u_+ to the orbital wave functions which are the basis functions appropriate to trigonal symmetry of the two-dimensional irreducible representation E of the cubic group. More specifically,

$$u_+ \sim -[(u+iv)/\sqrt{2}] \tag{24a}$$

and

$$u_- \sim +[(u-iv)/\sqrt{2}], \tag{24b}$$

where u and v transform like $z^2-\frac{1}{2}(x^2+y^2)$ and $(\frac{3}{2})\times(x^2-y^2)$, respectively. As there are no matrix elements of $\mathbf{L}$ within E, we have

$$g_{||}(\bar{E}) = 2\langle ^2E; u_-, +\tfrac{1}{2}|L_z+2S_z|^2E; u_-, +\tfrac{1}{2}\rangle = 2 \tag{25a}$$

and

$$\langle ^2E; u_-, +\tfrac{1}{2}|L_+ + 2S_+|^2E; u_+, -\tfrac{1}{2}\rangle = 0, \tag{25b}$$

from which it follows that $g_\perp = 0$. With $g_\perp = 0$, the sign of $g_{||}$ may be chosen positive or negative.

If one, however, considers the admixtures of higher $^2T_2(t_2{}^3)$ and $^2T_1$ states to ^2E by spin-orbit coupling and trigonal field, then one finds that the modified wave functions for $\bar{E}$ are given by

$$\begin{aligned}\bar{E}_-'(u_+ - \tfrac{1}{2}) = \alpha|u_+, -\tfrac{1}{2}\rangle + \beta|^2T_1, a_+, -\tfrac{1}{2}\rangle \\ +\gamma|^2T_1; a_0, +\tfrac{1}{2}\rangle + \delta|^2T_2; x_+, -\tfrac{1}{2}\rangle \\ +\epsilon|^2T_2; x_0, -\tfrac{1}{2}\rangle,\end{aligned} \tag{26}$$

and $\bar{E}_+'(u_- + \frac{1}{2})$ is the time reversed state. α is close to unity and $\beta, \cdots, \epsilon$ are small quantities. a_+, a_-, and a_0 are the three basic wave functions which comprise T_1, and x_0, x_+ and x_- those of T_2. More details are to be found in the work of Sugano and Tanabe[16] and in Imbusch *et al.*[17] With these modified wave functions, we now may make transitions between $\bar{E}_+'$ and $\bar{E}_-'$ with a transverse rf field h of the type

$$\langle \bar{E}_+'|h_+L_-|\bar{E}_-'\rangle,$$

which arise from

$$\langle u_-, +\tfrac{1}{2}|L_-|^2T_1; a_0, +\tfrac{1}{2}\rangle.$$

Here we make a transition from the lower Zeeman component $\bar{E}_-'$ to the upper one $\bar{E}_+'$ via h_+L_-, whereas h_-S_+ would be effective for normal spin states; thus the opposite sense of circular polarization produces the transition, and hence $g_{||}$ is negative. The magnitude of $g_{||}$ is also modified by the above admixtures so that $g_{||} = -2.44$. This modification of the magnitude of $g_{||}$ is primarily due to the terms with coefficients β and δ in Eq. (26), i.e., to orbital admixture with almost negligible modification of the spin state. The orbital admixture is represented by 0.44 and the negative sign of g is chosen in accord with the direction of precession. Under these circumstances, as outlined above, we expect a Kittel-Van Vleck relation to hold between g and g'. However, because of the necessity to choose $g_{||}$ negative to describe the fact that the opposite-sense of circularly polarized radiation is needed to induce the transition as compared to normal free electrons, the lower Zeeman component must be labeled $S_z' = +\frac{1}{2}$ and the upper one $S_z' = -\frac{1}{2}$, so that $S_z' = -\langle S_z\rangle$ and $\rho = -1$. In this case the relation between g and g' is given by

$$g' \sim g/(g+1). \tag{27}$$

C. Opposite Signs of $g_{||}$ and $g_{||}'$: Anisotropic g and Isotropic g'

The Ce^{3+} ion has a single unpaired f electron with angular momentum $L=3$. Spin-orbit coupling gives rise to the ground-state free-ion term $^2F_{5/2}$ and to the $^2F_{7/2}$ term some 5000 cm^{-1} away. In YES (yttrium ethyl sulphate), the Ce^{3+} enters substitutionally for the Y^{3+} at a site of point symmetry C_{3h}. This splits the $J=\frac{5}{2}$ manifold into three Kramers doublets characterized by $J_z = \pm\frac{5}{2}, \pm\frac{3}{2}$, and $\pm\frac{1}{2}$. The relative position and order of these doublets is determined by the relative strength and signs of the different crystal field terms. In both the concentrated CeES and the dilute Ce:YES the $|\pm\frac{5}{2}\rangle$ states lie lowest.[18] Under these circumstances, one expects $g_{||} = 2g_J\langle J_z\rangle$ and $g_\perp = 0$. In fact, however, one finds that $g_{||} = 3.810$ and $g_\perp = 0.20$. This small value of $g_\perp$ has been ascribed to two different possible sources. First, it has been suggested that the true site symmetry might be lower than C_{3h}, i.e., C_3, which would give rise to terms of the type $Y_4{}^3$ in the crystalline field potential, leading to a small admixture of $|\pm\frac{1}{2}\rangle$ states into the ground Kramers doublet, now given by

$$|b\rangle = 0.952|+\tfrac{5}{2}\rangle + 0.306|-\tfrac{1}{2}\rangle, \tag{28a}$$

$$|a\rangle = 0.952|-\tfrac{5}{2}\rangle + 0.306|+\tfrac{1}{2}\rangle. \tag{28b}$$

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[14] R. Huguenin and D. Baldock, Phys. Rev. Letters **16**, 795 (1966).

[15] A. M. Clogston, Phys. Rev. **118**, 1229 (1960).

[16] S. Sugano and Y. Tanabe, J. Phys. Soc. Japan **13**, 880 (1958).

[17] G. F. Imbusch, S. Chinn, and S. Geschwind, Phys. Rev. **161**, 295 (1967).

[18] G. H. Larson and C. D. Jeffries, Phys. Rev. **141**, 461 (1966).

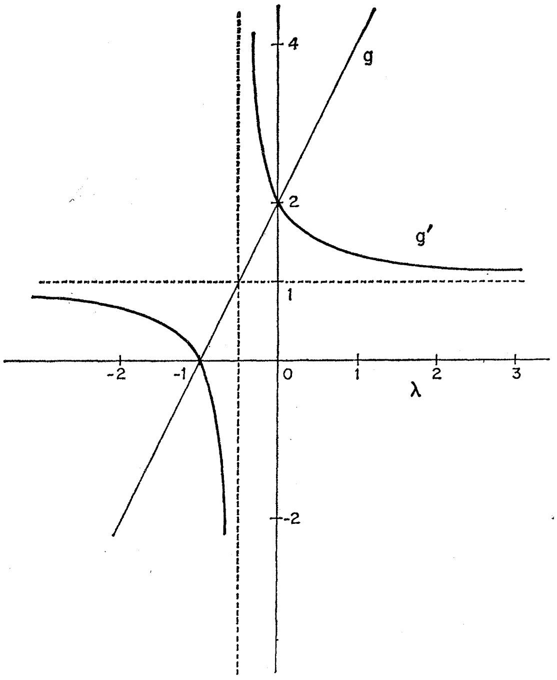

FIG. 1. Plot of the theoretical g and g' values near the center of the zone and for Γ_7 symmetry in a cubic semiconductor. $\lambda\hbar$ is the orbital angular momentum admixed by spin-orbit interaction.

Transitions can now be made from $|a\rangle$ to $|b\rangle$ via an r.f. perturbation of the form h_+J_- so that $g_\perp$ is no longer zero. Alternatively, one can still assume the true site symmetry to be C_{3h} but invoke the effect of the $V_6{}^6$ cubic crystal field term in admixing the $J=\frac{7}{2}$ manifold into the ground state, which as a result of this $V_6{}^6$ term can now be characterized by

$$|b\rangle=\alpha|\tfrac{5}{2},+\tfrac{5}{2}\rangle+\beta|\tfrac{7}{2},-\tfrac{7}{2}\rangle, \tag{29a}$$

$$|a\rangle=\alpha|\tfrac{5}{2},-\tfrac{5}{2}\rangle\beta|\tfrac{7}{2},+\tfrac{7}{2}\rangle, \tag{29b}$$

where $\alpha\gg\beta$.

Again we have a nonvanishing $g_\perp$ arising from

$$\langle\tfrac{5}{2},-\tfrac{7}{2}|h_+(L_-+2S_-)|\tfrac{7}{2},-\tfrac{5}{2}\rangle.$$

However, in either of the two cases above, the transition from the lower state $|a\rangle$ to $|b\rangle$ is made by h_+J_- or $h_+(L_-+2S_-)$ as opposed to h_-S_+ for normal electron spins, so that a negative $g_{\|}$ must be assigned to the transition. On the other hand, under the assumption that J is a good quantum number, $g'=+g_J=+6/7$. The fact that J is not a good quantum number when one considers the small admixture from the $J=\frac{7}{2}$ state has, nonetheless, a relatively small effect on $g_{\|}'$. (See note added in proof.)

D. Semiconductors with Very Large g

Another case where a modified Kittel-Van Vleck relation is obeyed, although g can be very different from 2, is that of electrons in the vicinity of the conduction-band minimum ($\mathbf{k}=0$, symmetry Γ_6) in a cubic semiconductor such as indium antimonide. To a very good approximation the wave function at $\mathbf{k}=0$ has s symmetry around each lattice site so that the spin-orbit interaction vanishes and the spin-degenerate Γ_6 states can be taken as pure spin up and pure spin down; we denote them by $|s_\uparrow\rangle$ and $|s_\downarrow\rangle$. The magnetic moment operator is $\boldsymbol{\mu}=-\beta(\mathfrak{L}+\boldsymbol{\sigma})$, where $\boldsymbol{\sigma}$ is, in units of $\hbar$, twice the spin moment, and $\mathfrak{L}$ is the periodic part of the orbital angular momentum operator, whose explicit expression need not be given here.[19] The transformation properties of $\mathfrak{L}$ under the cubic group are identical with those of $\boldsymbol{\sigma}$ (as is obviously necessary if $\mathfrak{L}+\boldsymbol{\sigma}$ is to have physical meaning), i.e., they both transform as Γ_4. There exists a generalization of the Wigner-Eckart theorem to finite groups,[20] and the condition for the theorem to apply in its simple form is that the representation of the operator ($\mathfrak{L}$ or $\boldsymbol{\sigma}$) be contained only once in the product of the representations of the two manifolds between which the matrix elements are taken. Since $\Gamma_6\times\Gamma_6=\Gamma_1+\Gamma_4$, this is the case here, and hence the matrices of $\mathfrak{L}$ and $\boldsymbol{\sigma}$ are related by

$$\langle\Gamma_6|\mathfrak{L}_i|\Gamma_6\rangle=\lambda\langle\Gamma_6|\sigma_i|\Gamma_6\rangle, \tag{30}$$

where $i=x, y, z$ and the proportionality constant λ gives the orbital moment induced by spin-orbit interaction.

Because of cubic symmetry, $\langle\Gamma_6|\boldsymbol{\sigma}|\Gamma_6\rangle$ is independent of the direction of quantization and the g factor is isotropic. With the basis $|s_\uparrow\rangle$ and $|s_\downarrow\rangle$ we have $\langle s_z\rangle=S_z'$ and hence $g=2(\lambda+1)$, $g'=(\lambda+1)/(\lambda+\frac{1}{2})$, and $g'=g/g-1$. We have plotted on Fig. 1 the values of g and g' as functions of λ, and we see that both can vary widely with λ.

Some words of explanation concerning the value of λ may be useful here since it might appear at first sight that because of the atomic s character of the Γ_6 states, λ would have to vanish. However, this is not the case because a Bloch electron cannot be localized on any one site but instead travels across the crystal. It is this interatomic current which is responsible for a nonvanishing λ here. In a magnetic field the electrons travel in very wide orbits and in the expression of the orbital moment $\boldsymbol{\mu}_{\text{orb}}=-(e/2c)(\mathbf{x}\times\mathbf{v})$, the smallness of $|\mathbf{v}|$ is balanced by the large value of $|\mathbf{x}|$. A detailed wave-packet argument[21] due to Herring shows that

$$\boldsymbol{\mu}_{\text{orb}}=-(e\hbar/2m_sc)\boldsymbol{\sigma}, \tag{31}$$

where the spin effective mass m_s depends on the band structure. If the band gap between the conduction and the p-like valence bands is small and the spin-orbit splitting of the valence bands is large in comparison, m_s takes values of the order of the orbital effective mass, which can be very small. From (1) and (2) we

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[19] E. I. Blount, Phys. Rev. **126**, 1636 (1962); L. M. Roth, J. Phys. Chem. Solids **23**, 433 (1962).

[20] See, for example, G. F. Koster, Phys. Rev. **109**, 227 (1958).

[21] Y. Yafet, *Solid State Physics*, edited by F. Sietz and D. Turnbull (Academic Press Inc., New York, 1963), Vol. 14, p. 93.

find that $\lambda=(m/m_s)$, where m is the free-electron mass; thus $|\lambda|$ can be quite large. In indium antimonide, $\lambda\approx-25$, $g\approx-50$, and $g'\simeq1$.

The above analysis can also be applied to the twofold degenerate Γ_7 band which is the split-off valence band. The only difference is that, due to the atomic p character of the orbitals, the expectation value of S_z is $\langle S_z\rangle=\frac{1}{3}S_z'$. Thus a modified Kittel-Van Vleck relation as in Eq. (22a) would obtain with $\rho=\frac{1}{3}$.

The validity of these relations between g and g' depends only on the smallness of matrix elements of the spin-orbit interaction that mix the two spin directions of the orbital state Γ under consideration in such a way that $\langle S_z\rangle$ is no longer S_z' or $(\frac{1}{3})S_z'$. For instance in the III–V semiconductors, the orbitals Γ_1 contain s and f atomic functions, the latter being admixed by the odd crystal potential; for the Kittel-Van Vleck relation to hold, the matrix element of the spin-orbit interaction between Γ_1 and the higher lying states containing f functions must be small compared to the distance in energy to these states (which is satisfied in practice). However, it does *not* have to be small compared to the band gap, which determines the effective masses and the orbital moment.

E. Multiplicities Greater than 2 and Thermal Averages

It has been assumed in our definition of the g value given by Eq. (17) that the splitting in a magnetic field of the manifold of states is described by a single g tensor. This will always be true for the Kramers doublets which we have used for illustrations up to this point. However, if one considers higher multiplicities such as the Γ_8 quartet ($^4A_2$) of the ground state of Cr^{3+} in octahedral coordination or of Co^{2+} in tetrahedral coordination then, as has been indicated by Bleaney,[22] and Koster and Statz,[23] additional terms involving H are needed in the spin Hamiltonian, i.e.,

$$\mathcal{H}=g^{(1)}\beta\mathbf{H}\cdot\mathbf{S}'+g^{(2)}\{H_xS_x'^3+H_yS_y'^3+H_zS_z'^3-\tfrac{1}{5}[3S'(S'+1)-1]\mathbf{H}\cdot\mathbf{S}'\}\,,\quad(32)$$

where $S'=\frac{3}{2}$. Thus two g values are needed in this case. For higher multiplicities more will be needed. Moreover, there will now be two g''s as well. If we label the states of the Γ_8 quartet $|-\frac{3}{2}\rangle$, $|-\frac{1}{2}\rangle$, $|+\frac{1}{2}$, and $|+\frac{3}{2}\rangle$, then the $|\pm\frac{3}{2}\rangle$ states will have one $g'_{\pm3/2}$ and the $|\pm\frac{1}{2}\rangle$ a different $g_{\pm1/2}'$. One can in principle express each of these g''s in terms of the g's. However, the relation will be a very sensitive function of cubic crystal field and spin-orbit coupling. In practice, in many cases such as that of the $^4A_2$ ground state of Cr^{3+} these extra terms in the Zeeman splitting are negligible and $g_{\pm3/2}'\simeq g_{\pm1/2}'$ as well, so that the simple relation of Eq. (1) will hold. In the event that one is dealing with a system of levels i which have different g_i''s, all of which are partially occupied, then the observed g' in a gyromagnetic experiment will obviously be the appropriate thermal average, i.e.,

$$g'=\left(\sum_i\langle M\rangle_ie^{-E_i/kT}\Big/\sum_i\langle J\rangle_ie^{-E_i/kT}\right)(2mc/e)\,.\quad(33)$$

Under such circumstances it becomes less meaningful to consider the connection between this thermally averaged g' and the various spectroscopic splitting factors that describe this collection of states.

IV. EFFECT OF EXCHANGE INTERACTIONS

Since measurements of the gyromagnetic ratio g' are usually made on magnetically ordered materials, a few remarks on the extension of the preceding considerations to exchange-coupled systems are in order.

A. Effect of Exchange Interactions in Insulators

It is straightforward to include exchange interactions in a spin-Hamiltonian description of the low-lying states of ions, since we merely need the operator equivalents in fictitious spin space of the single-ion spin and orbital angular momentum operators. The only point which concerns us is the relative magnitude of the exchange interaction and the crystal field splitting of the low-lying levels of the single-ion Hamiltonian. If the exchange interaction is small, then the fictitious spin may be chosen to be the same as for the lowest lying level. If the exchange interaction is large, however, it will be capable of mixing excited levels into the ground level. This mixing can be taken into account either by enlarging the magnitude of the fictitious spin to include the excited single-ion level or by calculating the change in composition of the ground level resulting from the admixture of excited states by the exchange interaction. In this regard we note that such admixtures can change g but not g' without changing the relative amounts of $|L|$ and $|S|$ making up the state. This would occur in the example given in Sec. II C of the Γ_6 and Γ_7 levels of Yb^{3+}. These two levels both arise from a $^2F_{7/2}$ state and hence have the same amount of L and S. Mixing one into the other will nevertheless change the g factor. We conclude that all of the single-ion examples given above still hold in the presence of exchange, provided that this exchange is not strong enough to admix higher crystal field levels. If it is sufficiently strong to do so, the single-ion calculation must be altered to take the admixture into account.

B. Effect of Exchange Interactions in Metals

Originally the Kittel-Van Vleck relation was proposed to correlate the shifts in the g and g' values from the free-spin value in metallic ferromagnets. The electron states in these metals are Bloch states and the previous discussion of electronic levels in terms of crystal field splittings becomes inappropriate. Instead, the band-

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[22] B. Bleaney, Proc. Phys. Soc. (London) **73**, 939 (1959).

[23] See, for example, G. F. Koster and H. Statz, Phys. Rev. **113**, 445 (1959).

width and its closely associated quantity, the Fermi energy, are the relevant energy parameters. In absence of spin-orbit coupling, the orbital moment is completely quenched at an arbitrary point in the zone, and so $g'=2$; exchange commutes with the Zeeman energy, and so $g=2$. Hence exchange by itself does not affect g or g', which is well known.

However, exchange does not commute with the spin-orbit energy and will therefore introduce corrections to the g and g'shifts caused by the latter. To our knowledge, the detailed nature of these corrections has not been worked out; preliminary estimates indicate that there are corrections to the shift δg of order $(\delta g)^2 F_F/J$ and $\delta g(J/E_F)^2$, where it is assumed that the ratio of the exchange integral J to E_F is large compared to δg. Exchange may also bring interband contributions but these have not been estimated. Usually exchange energies are only a fraction of the Fermi energy and perhaps also of the interband energies even though for d bands the latter are often quite small. One may hope then that the exchange corrections can be neglected and that the g and g' shifts can be calculated for noninteracting electrons. The spin-orbit coupling in the $3d$ series is less than 0.08 eV, while band-structure calculations[24] show that in the region of the zone occupied by the holes in nickel the average separation of the $3d$ bands is of order 0.5 eV. Hence a first-order treatment of spin-orbit coupling seems legitimate, resulting to that order in the equality $\langle S_z\rangle = S_z'$ and in the validity of the Kittel-Van Vleck relation. Recent experiments[25] indicate that this relation is very closely obeyed in iron and nickel.

C. Coupled Sublattice in Ferromagnetic Resonance

In the rare-earth iron garnets, the iron is considered to be one sublattice with magnetization $\mathbf{M}_A$ which is exchange coupled to the rare-earth sublattice with magnetization $\mathbf{M}_B$. Equations of motion are then written for this coupled two-sublattice system as follows:

$$d\mathbf{M}_A/dt=\gamma_A\mathbf{M}_A\times(\mathbf{H}+\lambda\mathbf{M}_B)\,, \tag{34}$$

$$d\mathbf{M}_B/dt=\gamma_B\mathbf{M}_B\times(\mathbf{H}+\lambda\mathbf{M}_A)\,. \tag{35}$$

Here λ = exchange constant describing the molecular field interaction between sublattices A and B:

$$\gamma_A=g_A(e/2mc)\,,$$
$$\gamma_B=g_B(e/2mc)\,,$$
$$\mathbf{H}=\text{externally applied field}.$$

These two coupled equations have two resonant frequencies. One of these usually falls at a frequency in the far infrared and is of the order of $\gamma\lambda M$, while the other falls at a lower frequency in the microwave region and to a high approximation is independent of λ. This microwave resonance is given by[26]

$$\omega=\gamma_{\text{eff}}\mathbf{H}\,, \tag{36}$$

where

$$\gamma_{\text{eff}}=\frac{M_A+M_B}{M_A/\gamma_A+M_B/\gamma_B}\,. \tag{37}$$

Several authors have adopted the practice of calling M_A/γ_A and M_B/γ_B the angular momentum J_A and J_B of sublattice A and B. However, we must emphasize that this is incorrect; γ_A and γ_B are not magnetomechanical ratios; they are really the spectroscopic splitting factor multiplied by $e/2mc$. The torques exerted by the crystal field have been absorbed into the γ_A and γ_B as we have outlined in the Introduction. γ_{eff} therefore measures a spectroscopic splitting factor and is not what will be observed in an Einstein–de Haas experiment. The true angular momentum for each sublattice may be written as $J_A=(M_A/\gamma_A)(g_A/g_A')$, etc., where g_A' is the magnetomechanical ratio given by Eq. (6).

A very interesting situation arises when one considers the large damping characteristic of rare-earth sublattices. The rare earths (with the exception of S-state ions) have exceedingly short relaxation times down to about 40°K. These relaxation times may be faster than any precessional frequency of the rare-earth sublattice in either the exchange field or the external field. Kittel[27] has pointed out that as a result of this damping the rare-earth sublattice does not respond to a torque as a normal gyroscopic system. In a gyroscopic experiment it may in effect be considered to carry no angular momentum but only its magnetization. In that limiting case M_B/γ_B in Eq. (37) which is proportional to J_B may be set equal to zero and

$$\gamma_{\text{eff}}=\frac{M_A+M_B}{M_A/\gamma_A}\,. \tag{38}$$

As one lowers temperature one will observe a g shift as the relaxation time becomes longer and M_B/γ_B must be included in γ_{eff}. On the other hand, even though J_B may be effectively zero in a resonance experiment when the relaxation time is very short, it will be effective in an Einstein–de Haas experiment. One would therefore see a temperature-dependent g but a temperature-independent g' over a certain temperature range.

V. CONCLUSION

We have considered the Kittel-Van Vleck relation between the splitting factor g and magnetomechanical ratio g' and have given a generalization to the case where orbital admixtures are not necessarily small and where the g factor may be negative. This generalization

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[24] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).

[25] G. G. Scott, Rev. Mod. Phys. **34**, 102 (1962).

[26] R. K. Wangsness, Phys. Rev. **91**, 1085 (1953).

[27] C. Kittel, Phys. Rev. **115**, 1587 (1959).

is almost tautological in character and is most useful when symmetry leads to a constancy of the parameter involved independent of the strength of crystalline fields.

Note added in proof. In the case of the mechanism (28), the relation (22) holds with a different ρ and g for each direction. We have in this case anisotropic g values with $g_{\parallel}$ negative and g' positive and isotropic. If (29) holds, however, g' will no longer be isotropic, since $g_{\perp}'$ depends entirely on matrix elements between different J levels. A measurement of $g_{\perp}'$ would therefore distinguish the two mechanisms for producing a nonzero $g_{\perp}$. We wish to thank Dr. M. E. Foglio for a communication on this point.

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APPENDIX

We wish to prove that for a Kramers doublet at a site of orthorhombic symmetry the g and g' "tensors" can be diagonalized and their principal axes are the twofold axes of the crystal.

Let x, y, z be the crystal axes and n, m, refer to one of them. Then the rotation operators $R_n(\pi)=e^{-i\pi J_n}$ commute with the Hamiltonian and hence they leave the space spanned by the two states of the Kramers doublet invariant. We can choose then as basis vectors $|u\rangle$ and $|v\rangle$ such that

$$R_z(\pi)|u\rangle=e^{-i\alpha}|u\rangle,\quad R_z(\pi)|v\rangle=e^{-i\beta}|v\rangle,$$

and, if K is the time-reversal operator,

$$K|u\rangle=-|v\rangle,\quad K|v\rangle=+|u\rangle.$$

Since the spin is half-integral, we must also have

$$R_z(2\pi)|u\rangle=-|u\rangle,\quad R_z(2\pi)|v\rangle=-|v\rangle.$$

It follows that

$$\alpha=\pm\tfrac{1}{2}\pi,\quad \beta=\pm\tfrac{1}{2}\pi.$$

Since time reversal commutes with rotations, we have

$$\begin{aligned}KR_z(\pi)|u\rangle&=Ke^{-i\alpha}|u\rangle=-e^{i\alpha}|v\rangle\\&=R_z(\pi)K|u\rangle=-R_z(\pi)|v\rangle=-e^{-i\beta}|v\rangle.\end{aligned}$$

Hence $\beta=-\alpha$.

We now show that the z component of any axial vector, e.g., L_z, is diagonal in $|u\rangle$, $|v\rangle$.

From the vector character it follows that

$$L_mR_n(\pi)=(2\delta_{mn}-1)R_n(\pi)L_m.$$

Consider now (u,L_zv):

$$(u,L_zv)=(R_z(\pi)u,R_z(\pi)L_zv)=e^{2i\alpha}(u,L_zv)=-(u,L_zv).$$

Hence (u,L_zv) vanishes. From the fact that time reversal anticommutes with L_n, it follows that

$$(u,L_zu)=-(v,L_zv)=\lambda_z.$$

We now turn to the L_x and L_y components. Applying $R_z(\pi)$ to both sides of (u,L_xu), we get

$$(u,L_xu)=-(R_z(\pi)u,L_xR_z(\pi)u)=-(u,L_xu).$$

Hence $(u,L_xu)=0=(v,L_xv)$. Similarly $(u,L_yu)=(v,L_yv)=0$. We choose the relative phases of $|u\rangle$ and $|v\rangle$ such that $(u,L_xv)=\lambda_x$ is real. We now show that $(u,L_yv)=i\lambda_y$ is pure imaginary. We apply $R_x(\pi)$ to both sides of (u,L_zu),

$$(u,L_zu)=(R_x(\pi)u,R_x(\pi)L_zu)=-(R_x(\pi)u,L_zR_x(\pi)u).$$

Hence,

$$\begin{aligned}R_x(\pi)|u\rangle&=e^{-i\delta}|v\rangle,\\R_x(\pi)|v\rangle&=-e^{i\delta}|u\rangle.\end{aligned}$$

To determine δ we apply $R_x(\pi)$ to both sides of (u,L_xv),

$$(u,L_xv)=(R_x(\pi)u,L_xR_x(\pi)v)=-e^{2i\delta}(v,L_xu)=\lambda_x.$$

Hence $e^{2i\delta}=-1$.

Finally,

$$\begin{aligned}(u,L_yv)=-(R_x(\pi)u,L_yR_x(\pi)v)&=+e^{2i\delta}(v,L_yu)\\&=-(v,L_yu)=-(u,L_yv)^*.\end{aligned}$$

Hence $(u,L_yv)=i\lambda_y$.

We have thus shown that in the $|u\rangle$, $|v\rangle$ basis, the matrix of any axial vector can be written as $\lambda_x\sigma_x+\lambda_y\sigma_y+\lambda_z\sigma_z$, and so both $\mathbf{L}+\mathbf{S}$ and $\mathbf{L}+2\mathbf{S}$ can be written in this form, i.e., g and g' have the same set of axes.