

## Standard-Basis Operator Method in the Green's-Function Technique of Many-Body Systems with an Application to Ferromagnetism

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(Received 3 August 1971)

A new formalism, using standard-basis matrix operators, is presented for the study of the collective excitations and the thermodynamic properties of an ensemble of identical interacting quantum-mechanical systems subsequently called "ions," each ion having discrete energy levels. A model Hamiltonian is formulated in terms of these operators. The Hamiltonian contains terms which express the interaction of the ion with the crystal field and the external fields as well as terms which arise from the mutual interaction of ions. Using the double-time temperature-dependent Green's-function technique, the equations of motion of the Green's functions of standard-basis operators are developed in the random-phase decoupling approximation. It is demonstrated that the temperature-dependent correlation functions of standard-basis operators, which are obtained from associated spectral Green's functions, lead to a set of equations that can be solved for the occupation probabilities of the single-ion energy levels. Hence, one can calculate the thermal-average expectation value of any quantum-mechanical operator representing a microscopic observable of a single ion, or a pair of ions (correlations). An important feature of the standard-basis matrix-operator formalism is that the single-ion terms, such as crystal field, molecular field, or external fields, are always treated exactly in any Green's-function decoupling scheme. In contrast, Green's-function methods which use angular momentum operators often necessarily treat single-ion terms in a decoupling approximation. As an example, the general standard-basis operator theory is applied to the Heisenberg ferromagnet in the presence of uniaxial single-ion crystal-field anisotropy, which has received extensive theoretical attention previously, with widely varying results.

### I. INTRODUCTION: INTERACTING SYSTEMS IN SOLIDS

The physical properties of crystals may often be explained by a model in which the crystal is considered an ensemble of identical ions. Each ion, in turn is considered as a system with a finite number of energy levels. In general, these are energy levels of electrons in unfilled shells, determined by the Coulomb potential produced by the nucleus, the inner electronic shells, and by an effective field produced by the other ions. Such an effective field is the crystal field or the Weiss molecular field. Important physical effects arise from interactions which cannot be represented by an effective field, i.e., correlations between ions. These broaden the single-ion levels into bands, thus playing a decisive role in determining the excitation spectrum of the crystal. Examples where this model is successful are the crystals of the rare-earth and actinide compounds.<sup>1-3</sup>

An ensemble of identical systems, each having  $p$  discrete energy levels, for which the above description is valid can be described by a model operator Hamiltonian. This contains sums of two types of operators, single-system and two-system operators. The single-system operators represent the interaction of the individual system with the effective field. A single-system operator may be written as a matrix of dimension  $p$  when expressed in terms of

the complete set of  $p$  states of the system. The two-system operators represent the interactions between the individual systems and are formed from the product of two single-system matrices multiplied by an appropriate interaction constant, e.g., the Coulomb exchange integral.

In the *operator-equivalent method*, which is often used to interpret spin-resonance experiments, the Hamiltonian is expressed as a sum of products of powers of the components of a fictitious (or actual) angular momentum operator.<sup>4,5</sup> We propose an alternate scheme, which has certain advantages over the operator-equivalent method, as will be stated in Sec. III.

In order to study the excitation spectrum and the thermodynamic properties of an ensemble of interacting systems at arbitrary temperature, it is common practice to employ double-time temperature-dependent Green's functions.<sup>6,7</sup> In these methods where the Hamiltonian of the ensemble is written in terms of the components of fictitious angular momentum operators, the single-system Green's functions are usually formed from powers of these components. The equation of motion of these Green's functions leads to an infinite set of linear algebraic equations which couple the single-system Green's functions to the higher-order  $n$ -system Green's functions.

At present, approximate solutions to this infinite

set are found by truncation processes<sup>8-12</sup> which decouple the equations to form a closed set that can be solved for the single-system Green's functions. The Fourier transforms of these Green's functions are related, through equations found in the literature (see Refs. 6 and 7), to corresponding temperature-dependent correlation functions, which determine many of the important thermodynamic properties of the ensemble. There are many problems associated with the various Green's-function decoupling schemes. The main problem is that one has as yet no exact knowledge of the error involved in decoupling and must rely on physical intuition and comparison with experiment to justify a particular decoupling. Subsidiary problems arise within particular decoupling schemes in which angular momentum operators are used because the Green's functions are often formed from a set of powers of angular momentum components, which is incomplete in the sense that it is not closed under commutation. In this case even the single-ion terms have to be decoupled, which could be treated exactly if a complete set were used. However, when a complete set of angular momentum operators is used one may arrive at a redundant set of equations from which some property of the ensemble is calculated, arbitrarily omitting certain equations to overcome the redundancy. It is the objective of this paper to introduce standard-basis operators. For an ensemble of systems having discrete energy levels, a general Hamiltonian containing single- and two-system operators can be written in a very simple form using standard-basis operators, and the Green's functions of these operators could enable one to solve a large class of excitation problems in solids in a well-defined and consistent manner.

In some cases, where a suitable expansion parameter can be identified, perturbation theory represents an important alternative technique for calculating the thermodynamic properties of an ensemble of interacting systems at finite temperature. To clarify the differences between the perturbational approach and the decoupling method developed here, we note that each standard-basis operator may be expressed as the product of an annihilation and a creation operator. Either boson or fermion operators may be used. Consequently, diagram techniques which have been worked out for bosons and fermions could be used to find perturbational results for interacting  $n$ -level systems. The isotropic Heisenberg ferromagnet<sup>13</sup> has been treated perturbationally using the reciprocal interaction volume as the expansion parameter.

## II. STANDARD-BASIS OPERATOR FORMALISM

The definition and fundamental mathematical properties of a particular set of linearly independent matrix operators will be formulated in this

section. The operators form a basis for the set of linear transformations on a vector space  $\mathcal{V}_p$  of finite dimension  $p$  over the field  $\mathfrak{F}$  of complex numbers. A vector in the space  $\mathcal{V}_p$  represents a state of a physical system, which has  $p$  discrete energy levels. (In the case of degenerate levels,  $p$  is the sum of the multiplicities of the levels.)

The set  $|\alpha\rangle$  with  $\alpha=1, \dots, p$  of  $p$  unit column vectors of the form

$$|\alpha\rangle = \{0, \dots, 1_\alpha, \dots, 0\} \quad \text{with } \langle \alpha | \beta \rangle = \delta_{\alpha\beta}, \quad (2.1)$$

where the label  $\alpha$  denotes the only nonzero component, constitutes the standard basis for  $\mathcal{V}_p$ .

Physically, the vector  $|\alpha\rangle$  can be thought of as a state vector describing a system in the state  $\alpha$ . The set of  $p$  linearly independent vectors  $|\alpha\rangle$  with  $\alpha=1, \dots, p$  forms a complete orthonormal set of states of the system. Hence, the most general state of the system is a linear combination of the vectors  $|\alpha\rangle$ , with complex coefficients.

Let  $\tau_p$  represent the set of linear transformations of  $\mathcal{V}_p$  into itself. It is well known that  $\tau_p$  is an associative algebra and that  $\tau_p$  is  $p^2$  dimensional over the field of complex numbers.<sup>14</sup> If  $\hat{A} \in \tau_p$ , one can write

$$\hat{A}|\beta\rangle = \sum_{\alpha=1}^p A_{\alpha\beta}|\alpha\rangle \quad \text{for } \beta=1, \dots, p. \quad (2.2)$$

The set of  $p^2$  complex numbers  $A_{\alpha\beta}$  completely describes the linear transformation  $\hat{A}$ .

The  $p$ -dimensional matrices  $\hat{L}_{\alpha\beta} \in \tau_p$ , which will be used in all subsequent calculations, are defined by the form

$$\hat{L}_{\alpha\beta} = \begin{bmatrix} 0 & \cdots & 0 \\ \cdots & 1_{\alpha\beta} & \cdots \\ 0 & \cdots & 0 \end{bmatrix} \quad \text{for } \alpha, \beta=1, \dots, p. \quad (2.3)$$

The subscripts  $\alpha$  and  $\beta$  indicate that the only nonzero element is in the  $\alpha$  row,  $\beta$  column position. In analogy with the labeling of  $|\alpha\rangle$  we shall refer to the operators  $\hat{L}_{\alpha\beta}$  as *standard-basis operators*.

It is clear from (2.3) that the  $p^2$  operators  $\hat{L}_{\alpha\beta}$  are linearly independent; hence the set  $\{\hat{L}_{\alpha\beta}\}$  forms a basis for  $\tau_p$ . Any matrix operator  $\hat{A} \in \tau_p$  may thus be written as a linear combination of the  $p^2$  operators  $\hat{L}_{\alpha\beta}$  with the matrix elements of  $\hat{A}$  as the expansion coefficients as follows:

$$\hat{A} = \sum_{\alpha, \beta} A_{\alpha\beta} \hat{L}_{\alpha\beta}. \quad (2.4)$$

Since any product of operators  $\hat{A}\hat{B}\cdots\hat{Z}$  is also an element of  $\tau_p$ , it may also be expanded as in (2.4).

In order to formulate the fundamental properties of the standard-basis operators we apply  $\hat{L}_{\alpha\beta}$  to an arbitrary standard-basis vector  $|\gamma\rangle$ . From the

definitions (2.1) and (2.3) we obtain the equation

$$\hat{L}_{\alpha\beta}|\gamma\rangle = \delta_{\beta\gamma}|\alpha\rangle, \quad (2.5)$$

where  $\delta_{\beta\gamma}$  is the Kronecker delta symbol. The adjoint operator  $\hat{L}_{\alpha\beta}^\dagger$  is defined by the equation

$$\hat{L}_{\alpha\beta}^\dagger \hat{L}_{\alpha\beta}|\beta\rangle = \hat{L}_{\alpha\beta}^\dagger|\alpha\rangle = |\beta\rangle. \quad (2.6)$$

Using the multiplication rule for  $\hat{L}_{\alpha\beta}$ , which is

$$\hat{L}_{\alpha\alpha} \cdot \hat{L}_{\beta\beta} = \delta_{\beta\alpha} \cdot \hat{L}_{\alpha\beta}, \quad (2.7)$$

it follows from (2.6) that the adjoint operator is

$$\hat{L}_{\alpha\beta}^\dagger = \hat{L}_{\beta\alpha}. \quad (2.8)$$

It is evident from (2.5) that relative to the basis  $|\alpha\rangle$ , with  $\alpha=1, \dots, p$ , the nondiagonal operators  $\hat{L}_{\alpha\beta}$  are nilpotent (i. e.,  $\hat{L}_{\alpha\beta}^2=0$ ) and that they act as raising or lowering operators when  $\alpha > \beta$  or  $\alpha < \beta$ , respectively. The interlevel transitions generated by these operators are shown schematically in Fig. 1. Setting  $\alpha$  equal to  $\beta$  in (2.5) yields an eigenvalue equation for the diagonal operators  $\hat{L}_{\beta\beta}$  with eigenvalues 1 or 0. The diagonal operators also satisfy all the requirements for projection operators. Using the multiplication rule (2.7) the commutator for the standard-basis operators is given by the simple relation

$$[\hat{L}_{\alpha\alpha'}, \hat{L}_{\beta\beta'}] = \delta_{\beta\alpha'} \cdot \hat{L}_{\alpha\beta'} - \delta_{\alpha\beta'} \cdot \hat{L}_{\beta\alpha'}. \quad (2.9)$$

To this point, the development in this section has been concerned with the properties of the standard-basis operators  $\hat{L}_{\alpha\beta} \in \tau_p$  applied to the state vectors  $|\alpha\rangle$  in the subspace of dimension  $p$  of a single system. In general we shall be dealing with an ensemble of  $N$  identical interacting systems, each having  $p$  energy levels. When the ensemble can be described by a wave function, the latter can be expanded in terms of a complete set of orthonormalized wave functions of the noninteracting systems. Each term of the ensemble wave function contains products of the wave functions for different noninteracting systems in different states. Different systems will be labeled by a superscript  $l$ ,  $m$ , or  $n$ , e. g., the state vector for the  $n$ th system is given by  $|\alpha\rangle^n \in \mathcal{V}_p^n$ . The operator  $\hat{L}_{\alpha\beta}^n \in \tau_p^n$  applied to a product of single-system state vectors has the following meaning:

$$\begin{aligned} \hat{L}_{\alpha\beta}^n |\gamma_1\rangle^1 \cdots |\gamma_n\rangle^n \cdots |\gamma_N\rangle^N \\ = |\gamma_1\rangle^1 \cdots \hat{L}_{\alpha\beta}^n |\gamma_n\rangle^n \cdots |\gamma_N\rangle^N. \end{aligned} \quad (2.10)$$

Since the operator  $\hat{L}_{\alpha\beta}^n$  operates only on the state vector of the  $n$ th system, it commutes with any  $\hat{L}_{\nu\mu}^m$ ,  $m \neq n$ , and we may generalize (2.9) to

$$[\hat{L}_{\alpha\alpha'}^m, \hat{L}_{\beta\beta'}^n] = \delta^{mn}(\delta_{\beta\alpha'} \cdot \hat{L}_{\alpha\beta'}^n - \delta_{\alpha\beta'} \cdot \hat{L}_{\beta\alpha'}^n). \quad (2.11)$$

If the single systems are ions at fixed sites on a

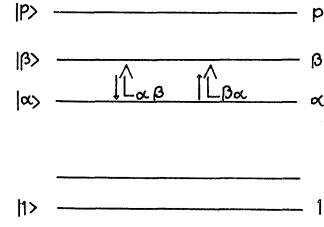


FIG. 1. The schematic diagram shows the set of energy levels of a quantum-mechanical system having  $p$  discrete energy levels. The standard-basis vector  $|\alpha\rangle$  represents the quantum-mechanical state vector  $|\alpha\rangle$  system in the energy state  $\alpha$ . The arrows  $\uparrow$  and  $\downarrow$  indicate interlevel transitions generated by the standard-basis operators  $\hat{L}_{\beta\alpha}$  and  $\hat{L}_{\alpha\beta}$ , respectively.

translationally invariant lattice, the nonzero thermal averages of the diagonal operators are independent of the ion site. In this case we introduce the notation

$$D_\alpha = \langle \hat{L}_{\alpha\alpha}^n \rangle, \quad (2.12)$$

where the bracket symbol  $\langle \cdots \rangle$  is defined by

$$\langle \hat{A} \rangle = \text{Tr} \hat{A} e^{-\hat{H}/k_B T} / \text{Tr} e^{-\hat{H}/k_B T}. \quad (2.13)$$

The Boltzmann constant is denoted by  $k_B$ , the absolute temperature by  $T$ , and the Hamilton operator of the ensemble by  $\hat{H}$ . As easily verified, the quantity  $D_\alpha$  represents the probability that the ion is in the state  $\alpha$ . From the definition (2.3) it is evident that the sum over all  $\hat{L}_{\alpha\alpha}$  is equal to the identity operator; hence, the sum of the occupation probabilities of all the levels is given by the normalization condition

$$\sum_{\alpha=1}^p D_\alpha = 1. \quad (2.14)$$

### III. ADVANTAGE OF USING STANDARD-BASIS OPERATORS

Standard-basis operators are naturally adapted to systems having discrete energy levels. They are represented by matrices whose elements are zero except for a single one, in contrast to the more complicated spin operators. They provide a clear picture of the interaction which causes interlevel transitions, obscured by the use of "fictitious angular momentum" operators. The diagonal standard-basis operators play the role of occupation-number operators for the individual levels, and the nondiagonal standard-basis operators act as raising or lowering operators which generate the interlevel transitions. Terms of the Hamiltonian which appear as single standard-basis operators, are, when expressed with help of operators of angular momentum of magnitude  $S = \frac{1}{2}(p-1)$ , sums of products of pow-

ers. Thus in order to utilize familiar angular momentum operators, one sacrifices simplicity and must deal with a complicated Hamiltonian.

Standard-basis operators have particularly simple commutation relations, making the calculation of the equations of motion trivial. In contrast to the case in which angular momentum operators are used, powers of operators higher than the first never appear in the equations of motion of standard-basis operators. Since standard-basis operators form a complete set, one can unambiguously apply interpolation decoupling techniques such as the random-phase approximation (RPA).<sup>8</sup> In the RPA, where the standard-basis operators are replaced by their thermal averages, a finite set of linear algebraic equations for the single-system Green's functions is derived from the general standard-basis operator Hamiltonian. As an example, this set has been solved for the  $S=1$  Heisenberg ferromagnet in the presence of uniaxial crystal-field anisotropy.

Analysis of all the correlation functions derived from a given set of coupled Green's functions shows that some of the correlation functions should be identically zero, in order to satisfy the multiplication rule (2.7) for the standard-basis operators. This rule is a mathematical guarantee that the following physical restrictions are enforced: (i) The system cannot be in different states at the same time, and (ii) no excitation energy can exceed the maximal eigenvalue of the Hamiltonian of the system. These restrictions can be formulated as a single equation with standard-basis operators as follows:

$$\langle \hat{L}_{\alpha_1 \beta_1}^n \hat{L}_{\alpha_2 \beta_2}^n \cdots \hat{L}_{\alpha_p \beta_p}^n \rangle = 0 \quad (3.1)$$

unless

$$\beta_i = \alpha_{i+1} \quad \text{for } i=1, \dots, p-1.$$

One may also say that every transition has to originate in the state where the previous transition ended. We shall call (3.1) the *monotopic restriction*, to emphasize that a system can occupy only one state at a given time. A special case of this restriction leads, in the case of spin waves, to the Dyson kinematic interaction.<sup>15,16</sup> This interaction arises from the fact that the spin of an ion cannot be flipped by more than  $2S$  units.

It is found that the Green's functions which lead to the physical quantities of interest can always be written in a form which ensures that neither the monotopic nor the kinematic restriction is violated. In the three-level ( $S=1$ ) ferromagnet, and in higher-spin ferromagnets not presented here, certain extraneous poles arise which do not occur in the usual RPA, which uses spin operators.<sup>17</sup> In the isotropic case these extraneous poles have the form of effective-field excitations in the spectral Green's

functions. These extraneous poles have no effect on the calculation of thermodynamic properties of the system if the monotopic restriction is observed. Similar poles were found by Murao and Matsubara,<sup>18</sup> who formed their Green's functions from components of both the angular momentum operator and the quadrupole moment operator. However, they did not take into account the monotopic restrictions which were obscured by their operator formalism, and they obtained entirely different thermodynamic properties from the ones obtained in this paper in Sec. IX.

#### IV. APPLICATION OF NEW FORMALISM TO AN ENSEMBLE OF IDENTICAL INTERACTING IONS IN A CRYSTAL

Assume  $\hat{A}_f^l$  and  $\hat{B}_g^l$  are quantum-mechanical operators, which act in the  $p$ -dimensional subspace of quantum-mechanical state vectors of the ion  $l$  with  $p$  energy levels. If the levels are degenerate,  $p$  is the sum of the multiplicities of all levels. These state vectors form a complete set which represent the states of an ion situated at the position  $\vec{x}_l$  on a translationally invariant lattice. The subscripts  $f$  and  $g$  denote the elements of the set  $\{\hat{A}_f^l; \hat{B}_g^l\}$ , e.g., the set might consist of components of the spin operator, which are given by  $\{\hat{S}_z^l, (\hat{S}_z^l)^2; \hat{S}_x^l, \hat{S}_y^l, \hat{S}_z^l\}$ . In terms of the operators  $\hat{A}_f^l$  and  $\hat{B}_g^l$ , our model Hamiltonian can in general be written in the form

$$\hat{H} = -\sum_l \hat{H}_0^l - \sum_{f;l} V_f \hat{A}_f^l - \frac{1}{2} \sum_{f,g;l,m} J_{f,g}^{l,m} \hat{B}_f^l \hat{B}_g^m. \quad (4.1)$$

The term  $\hat{H}_0^l$  is the "free"-ion Hamiltonian, whose eigenvalues are the energy levels  $\epsilon_\alpha$  ( $\alpha=1, \dots, p$ ) of the ion not interacting with any field or with other ions. The scalars  $V_f$  represent the strength of the effective field associated with the operators  $\hat{A}_f^l$ . For example, the numbers  $V_f$  might be the components of the external magnetic field, interacting through the inner product with the vector operator representing the angular momentum of the ion at the site  $\vec{x}_l$ . The scalars  $J_{f,g}^{l,m}$  are the interaction constants associated with the operator products  $\hat{B}_f^l \hat{B}_g^m$ , e.g., the numbers  $J_{f,g}^{l,m}$ , for fixed  $l$  and  $m$ , might be the components of an anisotropic-exchange tensor.

The expression of  $\hat{H}_0^l$  in terms of standard-basis operators is

$$H_0^l = \sum_\alpha \epsilon_\alpha \hat{L}_{\alpha\alpha}^l,$$

where the summation is over all  $p$  energy levels  $\alpha$  of the ion  $l$ . In accordance with (2.4) one can always expand the operators  $\hat{A}_f^l$  and  $\hat{B}_g^l$  in terms of standard-basis matrix operators. The coefficients in the expansions are the matrix elements  $A_{\alpha\alpha'}(f)$  and  $B_{\beta\beta'}(g)$  of the operators  $\hat{A}_f^l$  and  $\hat{B}_g^l$ , respectively. These matrix elements do not depend on the ion

label  $l$  because all ions in the crystal are assumed to be identical. Hence (4.1) becomes

$$\hat{H} = - \sum_{\alpha, l} \epsilon_{\alpha} \hat{L}_{\alpha\alpha}^l - \sum_{\alpha\alpha', l} h_{\alpha\alpha'} \hat{L}_{\alpha\alpha'}^l - \frac{1}{2} \sum_{\alpha\alpha', l} \sum_{\beta\beta', m} I_{\alpha\alpha', \beta\beta'}^{l, m} \hat{L}_{\alpha\alpha'}^l \hat{L}_{\beta\beta'}^m, \quad (4.2)$$

where  $h_{\alpha\alpha'}$  and  $I_{\alpha\alpha', \beta\beta'}^{l, m}$  are defined by

$$h_{\alpha\alpha'} = \sum_f V_f A_{\alpha\alpha'}(f) \quad (4.3)$$

and

$$I_{\alpha\alpha', \beta\beta'}^{l, m} = \sum_{f, g} J_{f, g}^{l, m} B_{\alpha\alpha'}(f) B_{\beta\beta'}(g). \quad (4.4)$$

The coupling constant  $I_{\alpha\alpha', \beta\beta'}^{l, m}$  has the properties

$$I_{\alpha\alpha', \beta\beta'}^{l, m} = I_{\beta\beta', \alpha\alpha'}(|\vec{x}_l - \vec{x}_m|) \quad (4.5)$$

and

$$I_{\alpha\alpha', \beta\beta'}^{l, l} = 0. \quad (4.6)$$

The first relation (4.5) expresses the translational invariance of the interaction Hamiltonian, and it shows that the interaction between identical ions in an ordered lattice depends only on the relative distance between the ions. Equation (4.6) expresses the fact that no ion interacts with itself.

For calculations to be carried out in the wave-vector representation, one defines the Fourier transform

$$I_{\alpha\alpha', \beta\beta'}^{l, m} = N^{-1} \sum_k I_{\alpha\alpha', \beta\beta'}^k e^{ik \cdot (x_l - x_m)} \quad (4.7)$$

and its inverse

$$I_{\alpha\alpha', \beta\beta'}^k = \sum_l I_{\alpha\alpha', \beta\beta'}^{l, m} e^{-ik \cdot (x_l - x_m)} \quad (4.8)$$

using

$$\delta^{lm} = N^{-1} \sum_k e^{ik \cdot (x_l - x_m)}. \quad (4.9)$$

In the above and in subsequent calculations, the letters  $k$  and  $q$  represent vectors of the first Brillouin zone of the reciprocal lattice. For convenience the vector notation is suppressed.

#### Effective-Field Hamiltonian in Terms of Standard-Basis Matrix Operators

In the spirit of the effective-field theory each ion in the crystal is to be treated as if it were responding to a field which is partly external and partly generated by the remaining ions. The interaction part (second term) of the Hamiltonian (4.1) can formally be separated into an effective-field term and a small interaction term by assuming that the expectations values of the operators  $\hat{B}_f^l$  deviate very little from their thermal averages.<sup>19</sup> We define the deviation operator  $\hat{\delta}_f^l$  by

$$\hat{\delta}_f^l = \hat{B}_f^l - \langle \hat{B}_f^l \rangle = \sum_{\alpha\alpha'} B_{\alpha\alpha'}(f) (\hat{L}_{\alpha\alpha'}^l - \delta_{\alpha\alpha'} D_{\alpha}), \quad (4.10)$$

where  $D_{\alpha}$  is defined by (2.12) and the symbol  $\langle \dots \rangle$  denotes the thermal average defined by (2.13). Let us introduce the set of numbers

$$c_{\nu\mu} = \sum_{\gamma} I_{\nu\mu, \gamma\gamma}^0 D_{\gamma} = \sum_{f, g} J_{f, g}^0 B_{\nu\mu}(f) \langle \hat{B}_g \rangle. \quad (4.11)$$

We shall denote

$$\hat{H}_e^l = - \sum_{\nu\mu} (\delta_{\nu\mu} \epsilon_{\nu} + h_{\nu\mu} + c_{\nu\mu}) \hat{L}_{\nu\mu}^l \quad (4.12)$$

the "effective-field Hamiltonian" in analogy to the well-known effective-field expression of magnetism. The distinguishing feature of the effective-field Hamiltonian is that it is linear in the single-ion operators instead of containing products of these operators. The coefficients  $c_{\nu\mu}$  are, of course, dependent on the thermal averages  $\langle \hat{B}_g \rangle$ . The term  $\delta_{\nu\mu} \epsilon_{\nu}$  arises from the Hamiltonian of the noninteracting ion. With these definitions and using (4.3), (4.4), and (4.5), the Hamiltonian (4.2) may be written in the form

$$\hat{H} = \frac{N}{2} \sum_{\alpha\beta} I_{\alpha\alpha, \beta\beta}^0 D_{\alpha} D_{\beta} + \sum_l \hat{H}_e^l + \sum_{l, m} \hat{H}_{\text{int}}^{l, m}, \quad (4.13)$$

where  $I_{\alpha\alpha, \beta\beta}^0$  is defined by (4.8). The last term in (4.12) is the small interaction term

$$\hat{H}_{\text{int}}^{l, m} = - \frac{1}{2} \sum_{f, g} J_{f, g}^{l, m} \hat{\delta}_f^l \hat{\delta}_g^m. \quad (4.14)$$

In cases where it is a reasonable assumption that  $\hat{H}_{\text{int}}^{l, m}$  can be neglected, at least as a first approximation, the problem of determining the ensemble energy spectrum is reduced to the diagonalization of  $\hat{H}_e^l$ , given by (4.12).

In formulating an approximation in which  $\hat{H}_{\text{int}}^{l, m}$  is not neglected, it is often useful to start with the effective-field eigenstates. We note that  $\langle \hat{\delta}_f^l \rangle = 0$ , a fact which is important in the development of the random-phase decoupling method in Sec. V.

#### V. GREEN'S FUNCTIONS OF STANDARD-BASIS OPERATORS

In this section we construct quantum-mechanical double-time temperature-dependent Green's functions from the standard-basis operators. The equations of motion of the spectral components of the two-operator Green's functions are formed using the general Hamiltonian (4.2). The three-operator Green's functions are decoupled in the random-phase approximation, yielding a general equation representing a finite set of coupled two-operator Green's functions.

The two-operator Green's function in the coordinate representation is denoted by

$$G_{\alpha\alpha', \beta\beta'}^{n, m}(t - t') = \langle\langle \hat{L}_{\alpha\alpha'}^n(t) | \hat{L}_{\beta\beta'}^m(t') \rangle\rangle, \quad (5.1)$$

where the double bracket  $\langle\langle \dots \rangle\rangle$  is defined by Zubarev.<sup>6</sup> This Green's function can be interpreted

physically as the probability amplitude that at time  $t'$  the  $m$ th ion makes a transition from the level  $\beta'$  to the level  $\beta$  followed at time  $t$  by a transition of the  $n$ th ion from the level  $\alpha'$  to the level  $\alpha$ . The spectral Green's function given by the Fourier time transform

$$G_{\alpha\alpha',\beta\beta'}^{n,m}(E) = \langle \langle \hat{L}_{\alpha\alpha'}^n | \hat{L}_{\beta\beta'}^m \rangle \rangle_E \\ = \int_{-\infty}^{\infty} \frac{dt}{2\pi} G_{\alpha\alpha',\beta\beta'}^{n,m}(t-t') e^{iE(t-t')} \quad (5.2)$$

is related to the two-operator time correlation function through the equation

$$\langle \hat{L}_{\beta\beta'}^m(t') \hat{L}_{\alpha\alpha'}^n(t) \rangle = \int_{-\infty}^{\infty} \frac{d\omega}{i} [\langle \langle \hat{L}_{\alpha\alpha'}^n | \hat{L}_{\beta\beta'}^m \rangle \rangle_{\omega-t'}]$$

$$E G_{\alpha\alpha',\beta\beta'}^{n,m}(E) = \frac{1}{2\pi} \langle [\hat{L}_{\alpha\alpha'}^n, \hat{L}_{\beta\beta'}^m] \rangle + (\epsilon_{\alpha} - \epsilon_{\alpha'}) G_{\alpha\alpha',\beta\beta'}^{n,m}(E) + \sum_{\nu} \{ h_{\nu\alpha} G_{\nu\alpha',\beta\beta'}^{n,m}(E) - h_{\alpha'\nu} G_{\alpha\nu,\beta\beta'}^{n,m}(E) \} \\ + \sum_{\nu\gamma\gamma'} \{ \hat{I}_{\nu\alpha,\gamma\gamma'}^{n,l} \langle \langle \hat{L}_{\nu\alpha'}^n \hat{L}_{\gamma\gamma'}^l | \hat{L}_{\beta\beta'}^m \rangle \rangle_E - I_{\alpha'\nu,\gamma\gamma'}^{n,l} \langle \langle \hat{L}_{\alpha\nu}^n \hat{L}_{\gamma\gamma'}^l | \hat{L}_{\beta\beta'}^m \rangle \rangle_E \}, \quad (5.6)$$

with the Greek subscripts ranging over the level indices from 1 to  $p$ , and the Latin superscripts ranging over the ion indices from 1 to  $N$ . Equation (5.6) shows explicitly that in general each two-operator Green's function is coupled to  $(2p-2)$  different two-operator Green's functions and also to  $(2p-1)p^2N$  three-operator Green's functions. Fortunately, in most problems the interlevel coupling is greatly reduced, as will be manifested by the absence of many of the interaction coupling constants in the Hamiltonian. The inter-ion coupling will be handled within the RPA by transforming the two-operator Green's functions to  $k$  space.

#### Application of RPA

The RPA is a well-defined linear operation in which thermal averages of products of operators are replaced by the product of their thermal averages. In accordance with this approximation, the three-operator Green's functions are reduced to two-operator Green's functions by the equation

$$\langle \langle \hat{L}_{\alpha\alpha'}^n \hat{L}_{\gamma\gamma'}^l | \hat{L}_{\beta\beta'}^m \rangle \rangle_E = \delta_{\alpha\alpha'} \langle \hat{L}_{\alpha\alpha'}^n \rangle G_{\gamma\gamma',\beta\beta'}^{l,m}(E) \\ + \delta_{\gamma\gamma'} \langle \hat{L}_{\gamma\gamma'}^l \rangle G_{\alpha\alpha',\beta\beta'}^{n,m}(E) + \delta^{nl} [\delta_{\gamma\alpha'} G_{\alpha\gamma',\beta\beta'}^{n,m}(E) \\ - \delta_{\alpha\gamma'} G_{\gamma\alpha',\beta\beta'}^{n,m}(E)]. \quad (5.7)$$

The last term in (5.7) arises from the commutation of  $\hat{L}_{\alpha\alpha'}^n$  with  $\hat{L}_{\gamma\gamma'}^l$ . This term will not contribute to

$$- \langle \langle \hat{L}_{\alpha\alpha'}^n | \hat{L}_{\beta\beta'}^m \rangle \rangle_{\omega+i0} ] f(\omega) e^{-i\omega(t-t')}. \quad (5.3)$$

The factor  $f(\omega)$  is the Bose function defined by

$$f(\omega) = (e^{\omega/k_B T} - 1)^{-1}. \quad (5.4)$$

The spectral components of the Green's function (5.1) satisfy the equation of motion

$$E G_{\alpha\alpha',\beta\beta'}^{n,m}(E) = (1/2\pi) \langle [\hat{L}_{\alpha\alpha'}^n, \hat{L}_{\beta\beta'}^m] \rangle \\ + \langle \langle [\hat{L}_{\alpha\alpha'}^n, \hat{H}] | \hat{L}_{\beta\beta'}^m \rangle \rangle_E. \quad (5.5)$$

The equation of motion of  $\hat{L}_{\alpha\alpha'}^n$ , appearing in the last term of (5.5) is to be calculated from the Hamiltonian (4.2). Using the commutator relation (2.11) and the symmetries of the interaction coupling constant gives

the equation of motion (5.6) because the multiplying factor  $\delta^{nl}$  generates interaction coupling constants referring to the same ion site, and these are zero.

Substituting (5.7) into (5.6) and expanding the commutator in the inhomogeneous term leads to the equation

$$(E - \epsilon_{\alpha} + \epsilon_{\alpha'}) G_{\alpha\alpha',\beta\beta'}^{n,m}(E) = \frac{\delta^{nm}}{2\pi} \delta_{\alpha\beta} \delta_{\beta\alpha'} D_{\alpha\alpha'} \\ + \sum_{\nu} [(h_{\nu\alpha} + c_{\nu\alpha}) G_{\nu\alpha',\beta\beta'}^{n,m}(E) \\ - (h_{\alpha'\nu} + c_{\alpha'\nu}) G_{\alpha\nu,\beta\beta'}^{n,m}(E)] \\ - D_{\alpha\alpha'} \sum_{\nu\mu l} I_{\alpha'\alpha,\nu\mu}^{n,l} G_{\nu\mu,\beta\beta'}^{l,m}(E), \quad (5.8)$$

where  $c_{\nu\mu}$  was defined by (4.11) and  $D_{\alpha\beta}$  is defined in terms of  $D_{\alpha}$  and  $D_{\beta}$  in (2.13) by

$$D_{\alpha\beta} = D_{\alpha} - D_{\beta}. \quad (5.9)$$

The Green's functions for different ion sites are decoupled by defining the Fourier transform

$$G_{\alpha\alpha',\beta\beta'}^{n,m}(E) = N^{-1} \sum_k \epsilon^{ik \cdot (\alpha_n - \alpha'_m)} G_{\alpha\alpha',\beta\beta'}^k(E), \quad (5.10)$$

and making use of the transforms (4.7) and (4.9). In  $k$  representation, Eq. (5.8) has the form

$$(E - \epsilon_{\alpha} + \epsilon_{\alpha'}) G_{\alpha\alpha',\beta\beta'}^k(E) = \frac{1}{2\pi} \delta_{\alpha\beta} \delta_{\beta\alpha'} D_{\alpha\alpha'}$$

$$\begin{aligned}
& + \sum_{\nu} [(h_{\nu\alpha} + c_{\nu\alpha}) G_{\nu\alpha',\beta\beta'}^k(E) \\
& - (h_{\alpha'\nu} + c_{\alpha'\nu}) G_{\alpha\nu,\beta\beta'}^k(E)] \\
& - D_{\alpha\alpha'} \sum_{\nu\mu} I_{\alpha'\alpha,\nu\mu}^k G_{\nu\mu,\beta\beta'}^k(E). \quad (5.11)
\end{aligned}$$

In (5.11) the Green's function  $G_{\alpha\alpha',\beta\beta'}^k(E)$  is expressed in terms of three different kinds of quantities. The last term on the right-hand side takes into account that part of the interaction between the ions which cannot be expressed in terms of an effective field. Dropping this last term would give  $N$ -fold-degenerate energy levels of the system without any dispersion, since  $I_{\alpha'\alpha,\nu\mu}^k$  is the only  $k$ -dependent coefficient in the equation. This is the effective- (or molecular-) field approximation of Sec. IV. Keeping this term will give rise to collective excitations, whose energies form bands, into which the  $N$ -fold-degenerate levels broaden. The second term on the right-hand side is the effective-field term. If the tensor  $h_{\nu\mu} + c_{\nu\mu}$  is diagonal the eigenstates in the effective field coincide with the states of the ensemble of free ions. In general the effective-field tensor is not diagonal, and diagonalization will precede the treatment of the interaction term. It serves to establish the temperature-dependent set of energy levels of each ion. The term on the left-hand side of (5.11) is always present, ensuring that the poles of the free-ion Green's function  $G_{\alpha\alpha',\beta\beta'}$  lie at  $E = \epsilon_{\alpha} - \epsilon_{\alpha'}$ .

The diagonalization aimed at establishing the effective-field levels of the ions can be carried out by dropping the last term in (5.11) and solving the resulting set of linear equations. These equations will have solutions only for certain eigenvalues  $E_{\alpha}$  of the secular equation. We will call the eigenstates of this truncated Hamiltonian (4.12) the effective-field eigenstates associated with the eigenvalues  $E_{\alpha}$ . In the effective-field eigenstates, Eq. (5.11) takes the simple form

$$\begin{aligned}
[E - E_{\alpha} + E_{\alpha'}] G_{\alpha\alpha',\beta\beta'}^k(E) + D_{\alpha\alpha'} \sum_{\nu\mu} M_{\alpha'\alpha,\nu\mu}^k G_{\nu\mu,\beta\beta'}^k(E) \\
= \frac{1}{2\pi} \delta_{\alpha\beta'} \delta_{\beta\alpha'} D_{\alpha\alpha'}, \quad (5.12)
\end{aligned}$$

where  $M_{\alpha'\alpha,\nu\mu}^k$  are the coupling constants in the new states. Equation (5.12) represents a set of a maximum of  $p^2$  coupled linear algebraic equations for the two-operator Green's functions, for every pair of values of the subscripts  $\beta$  and  $\beta'$ . Consider the special case when the original single-ion Hamiltonian is diagonal and when there is no multiplication in the interaction Hamiltonian of diagonal matrix elements of single-ion operators of one site with nondiagonal matrix elements of single-ion operators on another site. In this case the foregoing diagonalization process is unnecessary; the eigenvalues are

$$E_{\alpha} = \epsilon_{\alpha} + h_{\alpha\alpha} + c_{\alpha\alpha}, \quad (5.13)$$

and the coupling constants in (5.11) and (5.12) are the same. An example is the Heisenberg exchange Hamiltonian expressed in terms of the eigenfunctions of  $\hat{S}_z^n$ .

All equations derived from the Hamiltonian (4.2) were developed for a crystal having one translationally invariant lattice of  $N$  ions. These results can be easily generalized to the case of multiple sublattices, each containing  $N$  ions, by making the transformations  $l \rightarrow \sigma l$ ,  $m \rightarrow \rho m$ , etc., in all ion site superscripts. The Greek letters  $\sigma$  and  $\rho$  identify a given sublattice, and the letters  $l$  and  $m$  identify the ion sites within each sublattice. To accommodate the notational complications we make the following changes and definitions:

$$M_{\alpha\alpha',\beta\beta'}^k \rightarrow M_{\alpha\alpha',\beta\beta'}^{\sigma,\rho}(k), \quad (5.14)$$

$$G_{\alpha\alpha',\beta\beta'}^k(E) \rightarrow G_{\alpha\alpha',\beta\beta'}^{\sigma,\rho}(E, k) \quad (5.15)$$

and

$$D_{\alpha}^{\sigma} = \langle \hat{L}_{\alpha\alpha}^{\sigma,l} \rangle, \quad (5.16)$$

$$c_{\nu\mu}^{\sigma} = \sum_{\gamma,\rho} M_{\nu\mu,\gamma\gamma}^{\sigma,\rho}(0) D_{\gamma}^{\rho}. \quad (5.17)$$

In terms of the new definitions, the generalization of (5.12) to the case of multiple sublattices, each containing  $N$  ions, is given by

$$\begin{aligned}
[E - E_{\alpha}^{\sigma} + E_{\alpha'}^{\sigma}] G_{\alpha\alpha',\beta\beta'}^{\sigma,\rho}(E, k) + D_{\alpha\alpha'}^{\sigma} \sum_{\nu\mu,\tau} M_{\alpha'\alpha,\nu\mu}^{\sigma,\tau}(k) \\
\times G_{\nu\mu,\beta\beta'}^{\tau,\rho}(E, k) = \frac{\delta^{\sigma\rho}}{2\pi} \delta_{\alpha\beta'} \delta_{\beta\alpha'} D_{\alpha\alpha'}^{\sigma}. \quad (5.18)
\end{aligned}$$

It should be emphasized that (5.12) and (5.18) were obtained by the random-phase decoupling approximation applied only to the two-ion interaction terms in (5.6). The single-ion terms, such as the crystal field, molecular field, and external electric or magnetic fields, were treated exactly regardless of their magnitude relative to the two-ion terms. In contrast, an exact treatment of single-ion terms is not always possible using angular momentum operators. (See Sec. VII.)

## VI. OCCUPATION PROBABILITIES OF SINGLE-ION LEVELS AND CALCULATION OF OBSERVABLES

An important feature of the standard-basis operator formalism is that the occupation probabilities  $D_{\alpha}$  of the single-ion levels can be calculated directly from the spatial correlation functions corresponding to the equal-time Green's functions of the type  $G_{\alpha\beta,\beta\alpha}$ . To demonstrate this point, we note, that the solution of the coupled set of equations (5.12) can be written as

$$G_{\alpha\alpha',\beta\beta'}^k(E) = \frac{1}{2\pi} \sum_r a_r^k (E - \omega_r^k)^{-1}, \quad (6.1)$$

under the assumption that all roots  $\omega_r$  are simple. We have suppressed the subscripts  $\alpha$ ,  $\alpha'$ ,  $\beta$ , and  $\beta'$  of the coefficients  $a_r^k$ , which are independent of  $E$ .

By Fourier transforming (6.1) back to coordinate representation and making use of (5.3) with  $t = t'$ , we obtain the equal-time spatial correlation function associated with  $G_{\alpha\alpha',\beta\beta'}^{n,m}$ . It is given by

$$\langle \hat{L}_{\beta\beta'}^m \hat{L}_{\alpha\alpha'}^n \rangle = N^{-1} \sum_{k,r} a_r^k f(\omega_r^k) e^{ik \cdot (\alpha_n - \alpha'_m)}, \quad (6.2)$$

where  $f(x)$  is the Bose function (5.4). The correlation function  $\langle \hat{L}_{\beta\beta'}^m \hat{L}_{\alpha\alpha'}^n \rangle$  represents the probability that when the  $n$ th ion makes a transition from the level  $\alpha'$  to the level  $\alpha$ , the  $m$ th ion simultaneously makes a transition from the level  $\beta'$  to the level  $\beta$ . This correlation function is a measure of the strength of interaction between ions. If the interaction terms in (5.8) containing  $I_{\alpha'\alpha,\nu\mu}^{n,l}$  were neglected (this is the effective-field approximation), the Green's function  $G^{n,m}$  would not have been coupled to the Green's functions  $G^{l,m}$  for  $l = 1, \dots, N$ . In this case the correlation functions for  $m \neq n$  would all vanish.

The occupation probabilities  $D_\beta$  are obtained from the single-site correlation functions  $\langle \hat{L}_{\beta\alpha}^n \hat{L}_{\alpha\beta}^n \rangle = \langle \hat{L}_{\beta\beta}^n \rangle = D_\beta$ . Explicitly, from (6.2) we have that

$$D_\beta = N^{-1} \sum_{k,r} a_r^k f(\omega_r^k). \quad (6.3)$$

Examination of (5.12) shows that the right-hand side of (6.3) depends on the unknown probabilities  $D_r$  of the levels other than  $\beta$ . Hence, in general, one must solve a set of  $(p-1)$  coupled self-consistent equations in conjunction with the use of the normalization condition (2.14) to obtain each  $D_\beta$ .

Once the set  $D_1, D_2, \dots, D_p$  has been calculated, the problem of obtaining many of the thermodynamic properties of the ensemble has essentially been solved. Assume  $\hat{A}$  is a quantum-mechanical operator whose thermal average  $\langle \hat{A} \rangle$  represents some microscopic observable attributed to a single ion. If  $A_{\alpha\alpha}$  are the diagonal matrix elements of  $\hat{A}$  in some representation, then we have that

$$\langle \hat{A} \rangle = \sum_{\alpha=1}^p A_{\alpha\alpha} D_\alpha. \quad (6.4)$$

An example of such a thermal average is the single-ion magnetization determined by  $\langle S_x \rangle$ , where  $S_x$  is the component of the spin operator parallel to the direction of the bulk magnetization. Fortunately, in many problems the calculation of certain thermal averages can be accomplished by solving only one or two self-consistent equations for linear combinations of the occupation probabilities  $D_\beta$ .

As support for the effectiveness of the RPA Green's-function method of standard-basis operators, we consider the  $S=1$  Heisenberg ferromagnet with uniaxial crystal-field anisotropy.

#### VII. SPIN = 1 HEISENBERG FERROMAGNET WITH UNIAXIAL SINGLE-ION ANISOTROPY

Summary of Previous Work; Goal of Secs. VII, VIII, and IX

The thermodynamic properties of simple ferromagnets and antiferromagnets in the presence of single-ion uniaxial anisotropy have repeatedly been investigated using the Green's-function method.<sup>18,20-22</sup> The results derived from different decoupling schemes vary widely, as shown below.

In the approaches which use Green's functions formed from the components  $\hat{S}_+$ ,  $\hat{S}_-$ , and  $\hat{S}_z$  of the spin angular momentum operator, the Green's functions associated with the single-ion crystal-field terms are decoupled.<sup>20-22</sup> The RPA Green's function decoupling for  $S=1$  implies that correlation functions of the form  $\langle \hat{S}_z^m \hat{S}_z^n \hat{S}_z^l \hat{S}_z^k \rangle$  are replaced by  $\langle \hat{S}_z^l \rangle \langle \hat{S}_z^m \hat{S}_z^n \rangle$ . Here the superscripts label lattice sites. As explained by Lines,<sup>22</sup> for the case  $m \neq n \neq l$ , this approximation represents the neglect of certain correlations between  $\hat{S}_z^l$  and the spins on other lattice sites. However, in the exceptional case  $m = n = l$ , the above approximation is a statement concerning the thermal averages of the spin at a single site.

For the Green's functions arising from the Heisenberg exchange Hamiltonian, the coefficient of the terms with  $l = n$  is zero; hence the decoupling approximation for these Green's functions concerns the neglect of certain interspin correlations only. Inclusion of single-ion crystal-field terms in the Hamiltonian, however, changes the situation and raises the problem of decoupling terms for which  $l = n$ . Lines<sup>22</sup> devised a decoupling scheme for the single-ion terms which is essentially consistent with the decoupling of the exchange terms, i. e., the same amount of information is thought to have been retained in each case. However, in order to solve the resultant equations for the magnetization, Lines<sup>22</sup> made use of a theorem of Callen and Shtrikman<sup>23</sup> which is only valid in the limit of small single-ion anisotropy.

Recently, Murao and Matsubara<sup>18</sup> developed an approach in which the Green's functions are formulated in terms of the components  $\hat{S}_+$ ,  $\hat{S}_-$ , and  $\hat{S}_z$  of the spin operator and five components of the quadrupole moment tensor operator. (The latter are constructed from linear combinations of various products of the form  $\hat{S}_\alpha \hat{S}_\beta$ , where  $\alpha, \beta = +, -, \text{ or } z$ .) For  $S=1$  these operators form a complete set which is closed under commutation; hence they were able to apply their approach to the  $S=1$  ferromagnet with uniaxial crystal-field anisotropy. Since the un-



axial crystal-field term for  $S=1$  can be expressed in terms of the single component  $\frac{3}{2}\hat{S}_z^2 - 1$  of the quadrupole moment tensor operator, Ref. 18 obtained a random-phase decoupling approximation in which the crystal-field term was treated exactly, independent of the magnitude of the crystal field. However, the correlation functions needed to calculate the magnetization, susceptibility, etc., were overdetermined by a redundant set of equations. To obtain the pertinent correlation functions, they chose the "most interesting and physically appealing combination" of coupled Green's functions.

In the absence of crystal-field anisotropy, this combination leads to the Tahir-Kheli and ter Haar<sup>15</sup> RPA expression for  $\langle \hat{S}_z \rangle$  at low temperatures, with some additional terms containing an exponential temperature-dependent factor. In contrast, this same combination yields the Curie temperature that is predicted by the Weiss molecular-field model. Reference 18 states that Weiss-Curie temperature obtained from the "interesting combination" of Green's functions "seems to be a natural consequence of the RPA," and yet they point out that if they had chosen a different combination of Green's functions they would have obtained entirely different results.

In this section the standard-basis operator formalism developed in the RPA in Sec. V is applied to the problem considered also by Ref. 18. It is demonstrated that in the present formalism the pertinent correlation functions are not overdetermined, and that by satisfying the monotopic restrictions (3.1) the results of Tahir-Kheli<sup>15</sup> are reproduced in the isotropic case for the entire temperature range. Thus we are able to select the approximation from among the different published results which is consistent with the monotopic restrictions. Hence the main result of this section will be the establishment of a "credibility criterion" for different results obtained from the RPA.

#### Spin Hamiltonian for $S=1$

For  $S=1$  the Hamiltonian for the Heisenberg ferromagnet in the presence of uniaxial single-ion crystal-field anisotropy is given by

$$\hat{H} = -\sum_l [V(\hat{S}_z^l)^2 + h_z \hat{S}_z^l] - \frac{1}{2} \sum_{l,m} J^{l,m} [\hat{S}_z^l \hat{S}_z^m + \frac{1}{2}(\hat{S}_+^l \hat{S}_-^m + \hat{S}_-^l \hat{S}_+^m)]. \quad (7.1)$$

Here  $V$  is the crystal-field anisotropy constant,  $h_z$  is the external magnetic field times the Bohr magneton, and  $J^{l,m} = J(|\vec{x}_l - \vec{x}_m|)$  is the isotropic exchange constant. The summation is over all ions in the crystal. Because  $S=1$ , the anisotropy term cannot contain higher than quadratic terms of  $\hat{S}_z^l$ . Since the thermal average energy will not be cal-

culated here, constant terms were not included in the Hamiltonian (7.1).

Written relative to the complete set of states  $|\alpha\rangle$  defined in Sec. II, the spin operator components of the ion  $l$  for  $S=1$  are given in terms of the standard-basis operators by

$$\hat{S}_z^l = \hat{L}_{11}^l - \hat{L}_{33}^l, \quad \hat{S}_+^l = \sqrt{2} (\hat{L}_{12}^l + \hat{L}_{23}^l), \\ \hat{S}_-^l = \sqrt{2} (\hat{L}_{21}^l + \hat{L}_{32}^l). \quad (7.2)$$

Using (7.2) to rewrite the Hamiltonian (7.1) in terms of the standard-basis operators and comparing the new form with the general Hamiltonian (4.2), one obtains the quantities  $h_{\alpha\alpha'}$  and  $I_{\alpha\alpha',\beta\beta'}^{l,m}$ . They are given by

$$h_{11} = V + h_z, \quad h_{22} = 0, \quad h_{33} = V - h_z, \quad h_{\nu\mu} = 0 \\ \text{for } \nu \neq \mu \quad (7.3)$$

and

$$I_{11,11}^{l,m} = -I_{11,33}^{l,m} = I_{33,33}^{l,m} = I_{21,12}^{l,m} \\ = I_{21,23}^{l,m} = I_{32,12}^{l,m} = I_{32,33}^{l,m} = J^{l,m}. \quad (7.4)$$

From the definition (4.11) and (7.4) we find that

$$c_{11} = -c_{33} = J^0 D_{13}, \quad c_{22} = 0, \quad c_{\nu\mu} = 0 \\ \text{for } \nu \neq \mu, \quad (7.5)$$

where  $D_{13} = \langle \hat{L}_{11}^l \rangle - \langle \hat{L}_{33}^l \rangle$  and  $J^0$  is the  $k=0$  component of the Fourier transform  $J^k$  defined by

$$J^k = \sum_l J^{l,m} e^{-ik \cdot (x_l - x_m)}. \quad (7.6)$$

#### Effective-Field Results

For a preview of the physical properties of the system we begin with the effective-field model. Substituting the quantities in (7.3) and (7.5) into the effective-field Hamiltonian (4.12) yields

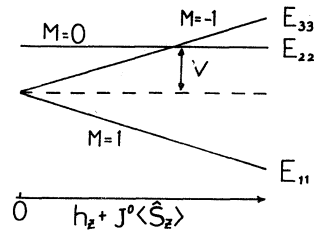


FIG. 2. The effective-field energy levels  $E_{11}$ ,  $E_{22}$ , and  $E_{33}$  are plotted vs the strength of the effective field  $h_z + J^0 \langle \hat{S}_z \rangle$  for the  $S=1$  Heisenberg ferromagnet with uniaxial crystal-field anisotropy  $V$ . The integers  $M=-1, 0$ , and  $1$  are the eigenvalues of the  $z$  component  $S_z$  of the spin operator.

$$\hat{H}_e^i = \sum_{\alpha} E_{\alpha\alpha} \hat{L}_{\alpha\alpha}^i, \quad (7.7)$$

where

$$E_{11} = -(V + h_{\mathbf{r}} + J^0 \langle \hat{S}_{\mathbf{r}} \rangle),$$

$$E_{22} = 0,$$

$$E_{33} = -(V - h_{\mathbf{r}} - J^0 \langle \hat{S}_{\mathbf{r}} \rangle). \quad (7.8)$$

The effective-field energy levels  $E_{\alpha\alpha}$  are shown diagrammatically in Fig. 2.

The thermal averages of  $\hat{S}_{\mathbf{r}}^i = \hat{L}_{11}^i - \hat{L}_{33}^i$  and  $(\hat{S}_{\mathbf{r}}^i)^2 = \hat{L}_{11}^i + \hat{L}_{33}^i$ , whose eigenvalues are 1, 0, -1, and 1, 0, 1, respectively, are given by

$$\left\langle \begin{array}{l} \hat{S}_{\mathbf{r}} \\ \hat{S}_{\mathbf{r}}^2 \end{array} \right\rangle = \frac{\exp[2(h_{\mathbf{r}} + J^0 \langle \hat{S}_{\mathbf{r}} \rangle) \theta^{-1}] \mp 1}{\exp[2(h_{\mathbf{r}} + J^0 \langle \hat{S}_{\mathbf{r}} \rangle) \theta^{-1}] + \exp[(-V + h_{\mathbf{r}} + J^0 \langle \hat{S}_{\mathbf{r}} \rangle) \theta^{-1}] + 1}. \quad (7.9)$$

The negative sign holds for  $\langle \hat{S}_{\mathbf{r}} \rangle$ , the positive sign for  $\langle \hat{S}_{\mathbf{r}}^2 \rangle$ . We use the notation  $\theta = k_B T$ . For arbitrary temperatures, the equation for  $\langle \hat{S}_{\mathbf{r}} \rangle$  requires a self-consistent solution. However, the Curie temperature  $\theta_C$  can be determined from the condition that  $\langle \hat{S}_{\mathbf{r}} \rangle \rightarrow 0$  at  $\theta_C$ . Setting the external field  $h_{\mathbf{r}} = 0$  we obtain from (7.9) the equations

$$\langle \hat{S}_{\mathbf{r}}^2 \rangle_{\theta=\theta_C} = \theta_C / J^0 = (1 + \frac{1}{2} e^{-V/\theta_C})^{-1}. \quad (7.10)$$

The Curie temperature can be obtained analytically for  $V/\theta_C \ll 1$  with the further restriction that  $V/J^0 \ll 1$ , we find, from (7.10), to order  $V/J^0$ , the dependence

$$\langle \hat{S}_{\mathbf{r}}^2 \rangle_{\theta=\theta_C} = \theta_C / J^0 = \frac{2}{3} (1 + \frac{1}{2} V/J^0). \quad (7.11)$$

It is interesting to note from (7.10) that  $\langle \hat{S}_{\mathbf{r}}^2 \rangle_{\theta=\theta_C}$  has the same dependence on the crystal-field anisotropy constant  $V$  as  $\theta_C/J^0$  (see Ref. 22.) Taking the limit  $V \rightarrow \infty$  in (7.10) and on the other hand the limit  $V \rightarrow 0$  in (7.11), one finds that the values of  $\langle \hat{S}_{\mathbf{r}}^2 \rangle = \theta_C/J^0$  lie in the interval  $(\frac{2}{3}, 1)$  for all  $V$ .

#### Calculation of the RPA Green's Functions of Standard-Basis Operators

The effective-field results do not depend on the details of the crystal lattice structure. This deficiency is remedied by using the RPA Green's-function approach which leads to structure-dependent collective excitations.

Substitution of the quantities in (7.3), (7.4), and (7.5) into the RPA equation of motion (5.12) using (5.13) yields the following sets of coupled equations for the spectral Green's functions:

$$[E - (V + h_{\mathbf{r}} + J^0 D_{13} - J^k D_{12})] G_{12,21}^k + J^k D_{12} G_{23,21}^k = D_{12}/2\pi, \quad (7.12)$$

$$J^k D_{23} G_{12,21}^k + [E - (-V + h_{\mathbf{r}} + J^0 D_{13} - J^k D_{23})] G_{23,21}^k = 0, \quad (7.13)$$

$$[E - (-V + h_{\mathbf{r}} + J^0 D_{13} - J^k D_{23})] G_{23,32}^k$$

$$+ J^k D_{23} G_{12,23}^k = D_{23}/2\pi, \quad (7.14)$$

$$J^k D_{12} G_{23,32}^k + [E - (V + h_{\mathbf{r}} + J^0 D_{13} - J^k D_{12})] G_{12,23}^k = 0, \quad (7.15)$$

$$[E - 2(h_{\mathbf{r}} + J^0 D_{13})] G_{13,31}^k = D_{13}/2\pi. \quad (7.16)$$

Comparison of (7.16) with (7.8) shows that the pole of  $G_{13,31}^k$  is at  $E = E_{33} - E_{11}$ , independent of  $k$ . This shows that the excitations between levels 1 and 3 are effective-field excitations in the RPA because the interaction part of the Hamiltonian (7.1) contains no matrix elements between these levels. A higher-order decoupling scheme, which takes into account the interaction between collective excitations is needed to produce dispersion in the pole of  $G_{13,31}^k$ .

The coupled equations (7.12)–(7.15) have unique solutions which can be written in the following form:

$$G_{12,21}^k(E) = \frac{D_{12}}{2\pi} \left[ \frac{A_k^- + B_k}{E - \omega_k^+} + \frac{A_k^+ - B_k}{E - \omega_k^-} \right] - G_{23,21}^k(E), \quad (7.17)$$

$$G_{23,32}^k(E) = \frac{D_{23}}{2\pi} \left[ \frac{A_k^- - B_k}{E - \omega_k^+} + \frac{A_k^+ + B_k}{E - \omega_k^-} \right] - G_{12,32}^k(E), \quad (7.18)$$

and

$$G_{23,21}^k(E) = G_{12,32}^k(E) = -\frac{D_{12} D_{23}}{2\pi} \beta_k^{-1} [(E - \omega_k^+)^{-1} - (E - \omega_k^-)^{-1}]. \quad (7.19)$$

Here the following abbreviations are used:

$$A_k^{\pm} = \frac{1}{2}(1 \pm D_{13} \beta_k^{-1}), \quad B_k = \frac{V}{J^k} \beta_k^{-1},$$

and

$$\beta_k = \left[ D_{13}^2 + 4 \frac{V}{J^k} \left( \frac{V}{J^k} + 3D_2 - 1 \right) \right]^{1/2}. \quad (7.20)$$

The roots  $\omega_k$  of the collective excitation spectrum are given by

$$\omega_k^\pm = h_\pm + \frac{1}{2}(2J^0 - J^k)D_{13} \pm \frac{1}{2}J^k \beta_k. \quad (7.21)$$

### VIII. ISOTROPIC CASE

For reasons of clarity and comparison with well-known results we shall first consider the isotropic special case of the more general problem exposed in Sec. VII. Setting  $V=0$  in (7.17)–(7.21) yields the simpler equations

$$G_{12,21}^k(E) = \frac{D_{12}}{2\pi}(E - \omega_k)^{-1} - G_{23,21}^k(E), \quad (8.1)$$

$$G_{23,32}^k(E) = \frac{D_{23}}{2\pi}(E - \omega_k)^{-1} - G_{12,32}^k(E), \quad (8.2)$$

and

$$\begin{aligned} G_{23,21}^k(E) &= G_{12,32}^k(E) \\ &= \frac{D_{12}D_{23}}{2\pi D_{13}} [(E - \omega_k)^{-1} - (E - E_0)^{-1}]. \end{aligned} \quad (8.3)$$

The excitation spectrum consists of a branch

$$\omega_k = h_\pm + (J^0 - J^k)D_{13} \quad (8.4)$$

and a single excitation of energy

$$E_0 = h_\pm + J^0 D_{13}. \quad (8.5)$$

The excitation  $\omega_k$  is the usual RPA spin-wave mode normalized by the temperature-dependent thermal average  $\langle S_\pm \rangle = D_{13}$ , and  $E_0 = E_{22} - E_{11} = E_{33} - E_{22}$  is a single-ion effective-field excitation as given by (7.8) with  $V=0$ .

In order to calculate the thermodynamic properties of the system we need to obtain the quantities  $D_\alpha$  for  $\alpha=1, 2$ , and  $3$ , which are the occupation probabilities of the three states corresponding to the projections  $M=-1, 0$ , and  $1$ , respectively, of the spin onto the axis of quantization ( $z$  axis). Two equations relating these unknown quantities can be found from the spatial single-site correlation functions associated with the Green's functions appearing on the left side of Eqs. (8.1) and (8.2). The third equation needed to determine each  $D_\alpha$  is given from (2.14) by the normalization condition

$$D_1 + D_2 + D_3 = 1. \quad (8.6)$$

The spatial correlation function associated with  $G_{12,21}^k$  is  $\langle \hat{L}_{21}^n \hat{L}_{12}^n \rangle$ . Setting  $n=m$  and using the multiplication rule (2.7) we obtain the occupation probability  $D_2 = \langle \hat{L}_{22}^n \rangle$  of the state  $M=0$ . Similarly, the correlation function associated with  $G_{23,21}^k$  is  $\langle \hat{L}_{21}^n \hat{L}_{23}^n \rangle$ . Since (8.1) has the form (6.1), we make use of (6.3) to obtain

$$D_2 = D_{12} \Phi - \langle \hat{L}_{21}^n \hat{L}_{23}^n \rangle. \quad (8.7)$$

Similarly from (8.2) and (8.3) we obtain

$$D_3 = D_{23} \Phi - \langle \hat{L}_{32}^n \hat{L}_{12}^n \rangle \quad (8.8)$$

and

$$\langle \hat{L}_{21}^n \hat{L}_{23}^n \rangle = \langle \hat{L}_{32}^n \hat{L}_{12}^n \rangle = \frac{D_{12}D_{23}}{D_{13}} [\Phi - f(E_0)], \quad (8.9)$$

where  $\Phi$  is defined by

$$\Phi = N^{-1} \sum_k f(\omega_k) = N^{-1} \sum_k (e^{\omega_k/\theta} - 1)^{-1}. \quad (8.10)$$

Use of the multiplication rule (2.7) shows that

$$\langle \hat{L}_{21}^n \hat{L}_{23}^n \rangle = \langle \hat{L}_{32}^n \hat{L}_{12}^n \rangle = 0. \quad (8.11)$$

Physically, this result is a manifestation of the monotopic restriction (3.1), which in this problem proscribes simultaneous occupation of more than one spin projection state. For example, if  $\langle \hat{L}_{21}^n \hat{L}_{23}^n \rangle$  were nonzero, it would imply that the  $n$ th spin could make simultaneous transitions from the states 1 and 3 to the state 2.

Contrary to the monotopic restriction is the fact that the right-hand side of (8.9) is not identically zero for an arbitrary choice of physical variables involved. Thus, it is evident that if the second term in (8.7) is replaced by the right side of (8.9), a different value is obtained for  $D_2$  than is obtained by enforcing the monotopic restriction, i. e., setting

$$\langle \hat{L}_{21}^n \hat{L}_{23}^n \rangle = 0. \quad (8.12)$$

[The enforcement is actually automatic when the Green's function (8.1) is used to obtain  $D_2$ .] One of the main merits of our method is that one can clearly recognize and fulfill the monotopic restrictions. With the monotopic restriction (8.12) enforced, Eqs. (8.6), (8.7) and (8.8) comprise a set of coupled linear algebraic equations which can be solved for the occupation probabilities of the spin projection states. Solving for  $D_1$  and  $D_3$  we recover the RPA results first derived by Tahir-Kheli and ter Haar,<sup>17</sup>

$$\langle \hat{S}_\pm \rangle = D_1 - D_3 = \frac{1 + 2\Phi}{1 + 3\Phi + 3\Phi^2}, \quad (8.13)$$

where  $\Phi$  is defined by (8.10).

The Curie temperature, found using (8.13), is

$$\theta_C/J^0 = \frac{2}{3} F^{-1} \quad \text{with } F = N^{-1} \sum_k (1 - J^k/J^0)^{-1}. \quad (8.14)$$

It should be noted that the Curie temperatures (8.14) calculated by the RPA are in remarkable agreement with the results of perturbation theory by Brown and Luttinger<sup>24</sup> and Domb and Sykes<sup>25</sup> (see Ref. 9). In contrast, molecular-field theory overestimates the ferromagnetic ordering and yields Curie temperatures that are as much as 33% higher than the results of perturbation theory.

We now apply the method of standard-basis operators to the anisotropic case, where no general results were available in the RPA.

## IX. ANISOTROPIC CASE

For the anisotropic case, let us return to Sec. VII. We enforce the monotopic restrictions, and obtain from (7.17) and (7.18), respectively, the relations

$$D_2 = D_{12} N^{-1} \sum_k [(A_k^- + B_k) f(\omega_k^+) + (A_k^+ - B_k) f(\omega_k^-)] \quad (9.1)$$

and

$$D_3 = D_{23} N^{-1} \sum_k [(A_k^- - B_k) f(\omega_k^+) + (A_k^+ + B_k) f(\omega_k^-)] . \quad (9.2)$$

Using (7.20), (7.21), (9.1), and (9.2), we obtain

$$\frac{D_2}{D_{12}} + \frac{D_3}{D_{23}} = P, \quad \frac{D_2}{D_{12}} - \frac{D_3}{D_{23}} = Q . \quad (9.3)$$

The quantities  $P$  and  $Q$  are given by

$$P = -1 + N^{-1} \sum_k [\sinh a_k + J^k D_{13} (2\theta b_k)^{-1} \sinh b_k] \times (\cosh a_k - \cosh b_k)^{-1} \quad (9.4)$$

and

$$Q = -(\theta N)^{-1} V \sum_k b_k^{-1} \sinh b_k (\cosh a_k - \cosh b_k)^{-1}, \quad (9.5)$$

where  $a_k$  and  $b_k$  are defined by

$$\theta a_k = h_{\mathbf{x}} + \frac{1}{2} (2J^0 - J^k) D_{13}, \quad \theta b_k = \frac{1}{2} J^k \beta_k . \quad (9.6)$$

Note, that (7.21) gives  $\omega_k^{\pm} = \theta(a_k \pm b_k)$ .

Adding and subtracting the equations in (9.3) yield the following relations for the occupation probabilities:

$$D_2 = \frac{1}{2} D_{12} (P + Q), \quad D_3 = \frac{1}{2} D_{23} (P - Q) . \quad (9.7)$$

Using the equations in (9.7) together with the normalization condition (8.6) to solve for  $D_1$  and  $D_3$  we find that  $\langle \hat{S}_{\mathbf{x}} \rangle = D_1 - D_3$  and  $\langle \hat{S}_{\mathbf{x}}^2 \rangle = D_1 + D_3$  are given by

$$\langle \hat{S}_{\mathbf{x}} \rangle = 4(1 + P) [1 + 3(1 + P)^2 + (2 - 3Q)Q]^{-1} \quad (9.8)$$

and

$$\langle \hat{S}_{\mathbf{x}}^2 \rangle = \frac{1}{3} \left( 2 + \frac{1 - Q}{1 + P} \langle \hat{S}_{\mathbf{x}} \rangle \right) . \quad (9.9)$$

It is also convenient to calculate the quantity  $Z = 1 - 3D_2 = 3\langle \hat{S}_{\mathbf{x}}^2 \rangle - 2$ , which appears implicitly in both  $P$  and  $Q$  through  $b_k$  and  $\beta_k$  [Eq. (7.20)]. From (9.9) we have that

$$Z = 1 - 3D_2 = \frac{1 - Q}{1 + P} \langle \hat{S}_{\mathbf{x}} \rangle . \quad (9.10)$$

For arbitrary temperatures,  $\langle \hat{S}_{\mathbf{x}} \rangle$  can be computed by solving the coupled equations (9.8) and (9.10) self-consistently using appropriate numerical techniques.

For low temperatures  $P$  and  $Q$  are approximately given by

$$P = N^{-1} \sum_k (1 + D_{13} \beta_k^{-1}) f(\omega_k^-), \quad (9.11)$$

$$Q = -N^{-1} \sum_k \frac{2V}{J^k} \beta_k^{-1} f(\omega_k^-) .$$

Expansion of  $\langle \hat{S}_{\mathbf{x}} \rangle$  from (9.8) in terms of  $P \ll 1$  and  $Q \ll 1$  yields to order linear in  $P$  and  $Q$  the relation

$$\langle \hat{S}_{\mathbf{x}} \rangle = 1 - \frac{1}{2} (P + Q) . \quad (9.12)$$

Substituting for  $P$  and  $Q$  from (9.11) gives

$$\langle \hat{S}_{\mathbf{x}} \rangle = 1 - N^{-1} \sum_k \frac{1}{2} \left[ 1 + \left( D_{13} - \frac{2V}{J^k} \right) \beta_k^{-1} \right] f(\omega_k^-) . \quad (9.13)$$

Since the right side of Eq. (9.13) contains both  $\langle \hat{S}_{\mathbf{x}} \rangle = D_{13}$  and  $Z = 1 - 3D_2$ , both of which approach 1 in the low-temperature limit,  $\langle \hat{S}_{\mathbf{x}} \rangle$  can be found iteratively using (9.10).

As a first iterative approximation for  $\langle \hat{S}_{\mathbf{x}} \rangle$  we set  $D_2 = D_3 = 0$  in (9.13) and find that

$$\langle \hat{S}_{\mathbf{x}} \rangle = 1 - N^{-1} \sum_k f(\omega_k^0), \quad (9.14)$$

with  $\omega_k^0$  given by

$$\omega_k^0 = V + h_{\mathbf{x}} + J^0 - J^k . \quad (9.15)$$

This is the spin-wave result obtained previously.<sup>26</sup> (For a complete mathematical and physical description of spin waves see Ref. 26.) The dispersion relation (9.15) shows that in the low-temperature spin-wave region the anisotropy acts like an external field and increases the  $k=0$  mode spin-wave energy gap.

Murao and Matsubara,<sup>18</sup> who obtained the same low-temperature result, point out that (9.14) is not valid if  $V/J^0 > 1$  because in this case  $\omega_k^0$  is not the lowest excitation. One can see from Fig. 2 that when  $V/J^0 > 1$  the lowest excitation is between the  $M = \pm 1$  levels. In RPA this excitation is of the single-ion type given by the pole of  $G_{13,31}^k$  in (7.16). In this case we find using (7.16) that in the low-temperature limit  $\langle \hat{S}_{\mathbf{x}} \rangle$  is given by

$$\langle \hat{S}_{\mathbf{x}} \rangle = 1 - e^{-2(h_{\mathbf{x}} + J^0)\theta^{-1}} . \quad (9.16)$$

The calculation of the Curie temperature  $\theta_C$  in the anisotropic case  $V \neq 0$  is complicated by the presence in  $\langle \hat{S}_{\mathbf{x}} \rangle$  of the nonzero unknown factor  $Z = 1 - 3D_2$ . From the level scheme in Fig. 2 it is evident that when the external field is zero ( $h_{\mathbf{x}} = 0$ ) the occupation probability  $D_2$  has the value  $\frac{1}{3}$  at  $\theta_C$  only in the limit  $V \rightarrow 0$ ; thus, in general,  $Z \neq 0$  at  $\theta_C$ .

In the limit  $\langle \hat{S}_{\mathbf{x}} \rangle \rightarrow 0$ , (9.4) and (9.5) become

$$P = -1 + \langle \hat{S}_{\mathbf{x}} \rangle X, \quad (9.17)$$

with  $X$  defined by

$$X = (2\theta_C N)^{-1} \sum_k (2J^0 - J^k + J^k b_k^{-1} \sinh b_k) (1 - \cosh b_k)^{-1} \quad (9.18)$$

and

$$Q = -(\theta_C N)^{-1} V \sum_k b_k^{-1} \sinh b_k (1 - \cosh b_k)^{-1}, \quad (9.19)$$

where

$$b_k = \theta_C^{-1} [V(V - J^k Z)]^{1/2}. \quad (9.20)$$

With the use of (9.8), (9.10), and (9.17) we obtain the equations

$$Q = 1 - XZ \quad (9.21)$$

and

$$Q = \frac{1}{3}(4Z^{-1} - 1). \quad (9.22)$$

In finding the relation (9.21), a constant root was rejected because  $Q$  becomes infinite as  $V \rightarrow 0$ , as can be verified from (9.19).

The Curie temperature  $\theta_C$  is obtained by eliminating  $Q$  and  $X$  from (9.21) and (9.22) using the definitions (9.18) and (9.19). The resulting equations must be solved self-consistently for the unknowns  $\theta_C$  and  $Z$ .

If the crystal-field anisotropy constant  $V$  is much less than  $\theta_C$ , the problem of obtaining the Curie temperature becomes considerably simplified. In this case  $b_k \ll 1$  and an expansion of (9.18) and (9.19) in terms of  $b_k$  shows that

$$X = -QR^{-1} \quad \text{where } R = V/J^0, \quad (9.23)$$

with  $Q$  given by

$$Q = 2\theta_C N^{-1} \sum_k (V - J^k Z)^{-1}. \quad (9.24)$$

Eliminating  $X$  and  $Q$  from (9.21), (9.22), and (9.23) and solving for  $Z$  gives to order  $R^2$

$$Z = R(1 - \frac{3}{4}R). \quad (9.25)$$

Equation (9.22) with (9.24) and using (9.25) yields the desired dependence of the Curie temperature on the ratio  $R = V/J^0 \ll 1$ :

$$\frac{\theta_C}{J^0} = \frac{2}{3} \left(1 - \frac{R}{4}\right) \left(N^{-1} \sum_k \frac{1}{(1 - \frac{3}{4}R)^{-1} - \gamma_k}\right)^{-1}$$

$$\text{with } \gamma_k = J^k/J^0. \quad (9.26)$$

For nearest-neighbor exchange in sc, bcc, and fcc lattices, the sum over  $k$  transforms into integrals of the extended Watson type which have been tabulated.<sup>27</sup> However, for an analytical comparison of the linear dependence of the Curie temperature on  $V/J^0$ , we expand (9.26) in terms of  $R$ , giving the result

$$\frac{\theta_C}{J^0} = \frac{2}{3} F^{-1} \left(1 + \frac{\frac{1}{2}(1 + \frac{3}{2}G/F)V}{J^0}\right) \quad (9.27)$$

with  $G = N^{-1} \sum_k \gamma_k (1 - \gamma_k)^{-2}$

and  $F$  is defined in (8.14).

In the absence of crystal-field anisotropy (9.27) becomes identical with the usual RPA result (8.14). Comparison of (9.27) with (7.11) shows that the leading dependence on  $V/J^0$  is the same as that obtained from the effective-field analysis. Using the relation  $Z = 3\langle \hat{S}_z^2 \rangle - 2$  and (9.25) we find that  $\langle \hat{S}_z^2 \rangle$  in the limit  $V/J^0 \ll 1$  is given by

$$\langle \hat{S}_z^2 \rangle = \frac{2}{3} (1 + \frac{1}{2} V/J^0). \quad (9.28)$$

This relation is identical with the effective-field result (7.11), in agreement with the result obtained by Lines<sup>22</sup> for  $S = 1$ .

This completes the analysis of the  $S = 1$  Heisenberg ferromagnet with uniaxial crystal-field anisotropy. In order to calculate the magnetization, Curie temperature, etc., for large values of the crystal-field energy, extensive self-consistent numerical calculations must be carried out.

#### ACKNOWLEDGMENTS

We are indebted to Dr. Y. L. Wang for useful discussions, and to the Sektion Physik der Universität München for their hospitality during the completion of the manuscript. This research was partially sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Grant No. AFOSR-69-1745.

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## Nuclear-Spin-Lattice Relaxation in Scandium Rare-Earth Alloys\*

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(Received 10 September 1971)

Scandium-base alloys of between 0.02 and 5.0 at. % cerium, gadolinium, and dysprosium have been studied using transient nuclear-magnetic-resonance techniques. The effect of the rare-earth solutes on the  $^{45}\text{Sc}$  linewidth and spin-lattice relaxation rate indicates that there are localized magnetic moments associated with gadolinium and dysprosium but not associated with cerium. For gadolinium and dysprosium concentrations less than 0.1 at. %, the linewidth is linear in the magnetization and described by the Ruderman-Kittle-Kasuya-Yosida predictions. For these alloys, the spin-lattice relaxation rate is described by  $1/T_1 = (1/T_1)_{\text{Sc}}[1 + KB_J(X)/H]$ , where  $(1/T_1)_{\text{Sc}}$  is the pure-scandium relaxation rate,  $K$  is a constant, and  $B_J(X)$  is the Brillouin function of  $X = gJ\mu_B H/(k_B T)$ . The  $T_1$  results are explained in terms of enhanced nuclear relaxation due to virtual excitation of the rare-earth moments. The linewidth, relaxation rate, and paramagnetic-moment enhancement for the dilute ScGd and ScDy alloys are consistent with a ratio for the effective  $s$ - $f$  interaction constants of  $(J_{sf})_{\text{Gd}}/(J_{sf})_{\text{Dy}} = 0.6 \pm 0.2$ . By comparison with the  $^{45}\text{Sc}$  results for the quadrivalent solutes titanium and thorium, it is found that cerium behaves as a quadrivalent solute in scandium.

### I. INTRODUCTION

Although the effect of magnetic impurities on the static response function of metals has been the subject of numerous investigations over the years, it has only been in the last few years that intense work on the dynamic response has taken place. Much of this work has delved into the difficult Kondo-effect problem in simple host metals. However, a clear study of the dynamic effects far removed from any Kondo regime is still necessary. For this reason, the present nuclear-magnetic-resonance (NMR) study of the effects of  $4f$  electron moments on metals was initiated.

The effects of dilute localized magnetic moments on the spin-lattice relaxation rate  $1/T_1$  of the host nuclear spins have been the subject of a number of experimental and theoretical investigations. Experiments performed at sufficiently low field on  $\text{CuMn}^1$  and  $\text{CdMn}^2$  yield results essentially in agreement with the theory proposed by Benoit, de Gennes,

and Silhouette (BGS).<sup>3</sup> This relaxation mechanism involves a simultaneous nuclear-spin-electron-spin flip, i. e., a *real* excitation of the impurity moment with energy conservation satisfied by the finite response of the electronic Zeeman transition at the NMR frequency. Experiments performed at high fields, where no significant overlap of the nuclear-resonance and electron-resonance response occurs on  $\text{CuMn}^4$  and  $\text{CdMn}^2$  yield results that have qualitative features in agreement with the theory proposed by Giovannini and Heeger (GH).<sup>5,6</sup> The GH mechanism involves a *virtual* excitation of the magnetic moment, which is then de-excited by the scattering of a conduction electron; this second-order process can interfere with the pure-metal Korringa<sup>7</sup> relaxation of the nuclear spins. However, the quantitative comparison<sup>2,6</sup> of the high-field relaxation data indicates an impurity contribution to the spin-lattice relaxation rate three orders of magnitude larger than that predicted by the GH theory.