iron-nickel alloys. We have obtained results similar to theirs for the concentration dependence of the spin magnetic moment. For the bcc phase, M_s for both Fe-Co and Fe-Ni may be expressed as a quadratic function of Z, where the ratios of the coefficients for the two alloys is constant at approximately 1.85 (see caption of Fig. 2). The values of M_s for the fcc region are linear in Z with slope -1.01 per electron added, in reasonable agreement with the values reported by Meyer and Asch[7] (-1.05). The intercept $M_s = 0$ occurs at $Z = 28.55$.

The results for the spin magnetization in the bcc region previously reported by Crangle and Hallam[9] are difficult to interpret. Their value seems too high, since, if we assume the magnetic moments are distributed among the atoms in the same manner before and after alloying (and consider that each atom acts individually), their results would require 3.2 ± 0.1 magnetic electrons to be carried by the nickel atom to be

consistent with the initial value of the slope. Our result reduces this number to $(1.1 \pm 0.1)\mu_B$ per atom.

RELATIONSHIP TO THEORETICAL CALCULATIONS

Using a band model, Mott[8] has calculated the total number of "holes" in iron to be 2.9 per atom, on the basis of a value of $2.1\mu_B$ for unbalanced spin with an orbital contribution of $0.12\mu_B$. Our value of M_0 of $0.092\mu_B$ changes Mott's results to 2.93 holes. This change will be significant when and if the uncertainty in the value of the polarization of the d bands is reduced.

Note added in proof. A. J. P. Meyer has pointed out in a private communication to the authors that the values of M_s and M_0 from Meyer and Asch[7] were obtained using M_t values for 0°K, whereas the M_0 and M_s reported here were obtained using values of M_t for 300°K.

Theory of Ferro- and Antiferromagnetic Resonance in Solids Containing Ions of Complicated Level Structure*

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(Received 13 January 1969)

The time-dependent molecular-field (TDMF) approach to magnetic resonance is described and illustrated with six examples. For the simplest models, the random-phase approximation of TDMF is equivalent to Tyablikov spin waves. However, whereas Green's function and spin-wave techniques are forced into same-site decorrelation approximations when confronted with complicated single-ion dynamics, TDMF is general enough to include any single-ion terms without difficulty. Ions appear as coupled oscillators whose allowed transitions are pulled in forming collective modes. The procedure, being quite general, is readily automated and is thus convenient in actual calculations for physical problems.

I. INTRODUCTION

THERE is an enormous body of literature concerning excitations from ordered magnetic configurations.[1] Much of it aims at the difficult many-body aspects, restricting attention to simple Hamiltonians.[2] When the temperature is not zero, many methods are for static properties only.[3] For the dynamics of Hamiltonians containing single-ion terms, that is, complicated Hamiltonians, at finite temperatures there are few

available techniques.[4,5] The best of these may be called the "time-dependent molecular-field" (TDMF) decoupling scheme. This paper is a description of that technique.

The TDMF has been used for treating rare-earth ions in the iron garnet,[6] but apparently its generality has not been widely appreciated.[7] The method can, within the same approximation, treat Hamiltonians consisting of exchange[8] plus one-ion terms of *arbitrary complexity*.

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* Part of this work was done at Osaka University, Toyonaka, Japan, under the auspices of the U. S.-Japan Cooperative Science Program, and part was done at Yale University with partial support from the National Science Foundation.

[1] See F. Keffer, in *Handbuch der Physik*, edited by H. P. J. Wijn (Springer-Verlag, New York, 1966), Vol. XVII/2, p. 28 ff.; S. Foner, in *Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. I, p. 383 ff, for many references.

[2] For example, R. A. Tahir-Kheli, Phys. Rev. 159, 439 (1967).

[3] For example, B. Srieb, H. B. Callen, and G. Horwitz, Phys. Rev. 130, 1798 (1963); also review by M. Fisher, Rept. Progr. Phys. XXX/II, 615 (1967).

[4] B. R. Cooper, R. J. F. Elliot, S. J. Nettel, and H. Suhl, Phys. Rev. 127, 57 (1962).

[5] Y. Ebina, Phys. Rev. 153, 561 (1967); T. Murao and T. Matsubara (unpublished report).

[6] F. Hartmann-Boutron, Compt. Rend. 256, 4412 (1963); Physik Kondensierten Materie 2, 80 (1964); J. F. Dillon and L. R. Walker, Phys. Rev. 124, 1401 (1961); J. H. Van Vleck and R. Orbach, Phys. Rev. Letters 11, 65 (1963); R. Alben, Phys. Rev. 167, 249 (1968).

[7] Recent applications by the author are R. Alben, J. Phys. Soc. Japan 26, 261 (1969); J. Appl. Phys. 40, 1112 (1969).

[8] The present work considers the common case of bilinear exchange. More complicated couplings may be handled by TDMF although at a considerable loss of efficiency.

The decoupling is of the RPA[9] (random-phase approximation) type and is fully as good as linear spin-wave theory in treating exchange. Both spin-wave-like and single-ion-like normal modes appear. Importantly, TDMF is easy to apply and in the many cases where single-ion effects are large, it should prove of considerable value.

In Sec. II, we begin discussing the theory itself, first in the restricted class of problems to which it has been traditionally applied. Then we assume a particular point of view and arrive at a formulation suited for applications to complicated Hamiltonians. In Sec. III, we give examples focusing on different implications of the theory and illustrating its results. Lastly, in Sec. IV, we present comments not covered by the examples and then conclude.

II. THEORY

This section contains four subdivisions: (A) gives the semiclassical theory of magnetic resonance and elucidates the role of TDMF's in sublattice equations of motion. (B) shows how the same theory looks in the language of single-ion susceptibilities. These first two subsections describe concepts which have been used for many years; TDMF is not a new approach.

(C) and (D) describe the TDMF method for a more complicated quantum mechanical system. No new concepts are introduced, just matters of formulation. (C) considers briefly the equation of motion of formalism, awkward for complicated Hamiltonians. (D) contains a single-ion susceptibility formulation which is readily amenable for applications.

A. Time-Dependent Molecular Fields in Classical Theory

Although many of us are more familiar with static, Weiss molecular fields, TDMF's are a concept much used in magnetism.[10] Just as the Weiss field consists of an effective magnetic field proportional to a static magnetization,[11] a TDMF is an effective field similarly related to a changing magnetization.

Consider the following equation of motion for a sublattice magnetization:

$$\dot{\mathbf{M}}_i = \gamma \mathbf{M}_i \times (\mathbf{H} + \sum_j \lambda_{ij} \mathbf{M}_j), \qquad (1)$$

where H is an external field, λ_{ij} is an exchange coupling parameter between the i and j sublattices, M_i is the magnetization of the ith sublattice—a number in this

classical theory. The quantity $\lambda_{ij} M_j$ is then the molecular field (MF) due to j which acts on i. Since equations such as Eq. (1) are easily solved only for small disturbances, it is expedient to make a distinction between the static- and time-dependent parts of $\lambda_{ij} M_j$. The static parts are just the Weiss fields in the "quiet" configuration. The dynamic parts are associated with the modes of oscillation. The equations may be solved exactly for small disturbances; we write $\delta \mathbf{m}_i$ for small deviations in M_i and consider a harmonic mode

$$\mathbf{M}_i = \bar{\mathbf{M}}_i + \delta \mathbf{m}_i(t), \qquad (2)$$

$$\delta \mathbf{m}_i(t) = \delta \mathbf{m}_i e^{-i\omega t}.$$

Substituting Eq. (2) in Eq. (1) and eliminating second-order δ quantities, give the secular equations whose solutions give eigenfrequencies and modes.

For physical applications, it is more realistic in Eq. (1) to let i and j run over lattice sites; the exchange interaction is really short range. This new problem is also easily solved for small disturbances—let $m_{(i)}$ and $n_{(j)}$ be the mth and nth sites, respectively, on the ith and jth sublattices. Substitute in Eq. (1)

$$\delta \mathbf{m}_{n(i)} = \frac{1}{\sqrt{N_i}} \sum_k \delta \mathbf{m}_i(\mathbf{k}, \omega) e^{i(-\omega t - \mathbf{k} \cdot \mathbf{R}_{n(i)})}, \qquad (3)$$

where N_i is the number of sites on i, $\mathbf{k}$ runs over the Brillouin zone, and $\mathbf{R}_{n(i)}$ is the lattice vector to $n_{(i)}$. The eigensolutions are the spin-wave bands. A well-known example of this sort of calculation is Harris's work on spin waves in yttrium iron garnet (YIG).[12] Linearized boson equations of motion are also essentially the same.[13]

B. Single-Ion Susceptibilities for Classical Theory

Equation (1) may be solved by another method; that of sublattice or single-ion linear susceptibilities. An example should suffice.

First, take a magnetic moment, magnitude M_0, in a static magnetic field $\hat{k} H_0$. Its linear response (δm) to a transverse field $[h(\hat{\imath} \cos\omega t - \hat{\jmath} \sin\omega t)]$ may be written

$$\delta m^+ = \chi^+(\omega) h^+ e^{-i\omega t}, \qquad (4)$$

where

$$\delta m^+ = \delta m^x + i\delta m^y,$$

and

$$\chi^+(\omega) = M_0 / (H_0 - \omega/\gamma); \qquad (5)$$

$\chi^+(\omega)$ is a linear susceptibility. Next consider the "anisotropy field" model of a two-sublattice uniaxial antiferromagnet.[10] Let the static external magnetic field be zero, but allow for a transverse exciting external field. Each sublattice may be treated like the magnetic mo-

[9] D. Bohm and D. Pines, Phys. Rev. **92**, 609 (1953); F. Englert, Phys. Rev. Letters **5**, 102 (1960). For a discussion of the relation of RPA and time-dependent self-consistant fields (such as TDMF) see H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

[10] Some examples are F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952); M. Tinkham, *ibid.* **124**, 311 (1961); R. K. Wangsness, *ibid.* **119**, 1496 (1960).

[11] J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Philadelphia, 1966).

[12] A. B. Harris, Phys. Rev. **132**, 2398 (1963).

[13] The frequencies and modes arrived at in the linear boson formalism are identical to the semiclassical results. One may, however, discuss a nonclassical spin contraction due to zero-point motion when using the boson approach. See Ref. 14.

ment in Eq. (4) where now H_0 is the sum of exchange and anisotropy fields; h is now a sum of external field and TDMF's. Letting δm_u^+ refer to up and δm_d^+ to down sublattices, we have

$$\delta m_u^+ = \frac{M_0}{\lambda M_0 + H_A - \omega/\gamma}(h'e^{-i\omega t} - \lambda \delta m_d^+),$$

$$\delta m_d^+ = \frac{M_0}{\lambda M_0 + H_A + \omega/\gamma}(h'e^{-i\omega t} - \lambda \delta m_u^+),$$
(6)

where λ is the exchange constant (intersublattice only and positive antiferromagnetic), H_A is the anisotropy field, and M_0 is the sublattice magnetization (positive). h' is the external exciting field alone. The solution for δm's as function of h' is

$$\delta m_u^+ = h'e^{-i\omega t}\frac{M_0(H_A + \omega/\gamma)}{H_A(2\lambda M_0 + H_A) - (\omega/\gamma)^2},$$

$$\delta m_d^+ = h'e^{-i\omega t}\frac{M_0(H_A - \omega/\gamma)}{H_A(2\lambda M_0 + H_A) - (\omega/\gamma)^2}.$$
(7)

If we define $\delta m^+ = \delta m_u^+ + \delta m_d^+$, the net oscillating moment, we have

$$\delta m^+ = \Xi(\omega)h'e^{-i\omega t},$$

$$\Xi(\omega) = \frac{2M_0 H_A}{H_A(2\lambda M_0 + H_A) - (\omega/\gamma)^2}.$$
(8)

The quantity $\Xi_{(\omega)}$ is a net susceptibility of the system to external fields alone. It is not the same as the single-ion susceptibilities in Eq. (6); its poles are at different frequencies. It is Ξ, which is actually measurable. This is in direct analogy to the coupling together of mechanical or electrical oscillators.

The result [Eq. (8)] is the well-known one for this problem. Usually, it is gotten by the equation-of-motion formalism, fully equivalent to this susceptibility approach. To relate Eq. (8) to the question of normal modes, recall that a normal mode is a self-sustaining motion when no forcing term is present. As $h' \to 0$, only modes such that $\omega/\gamma = \pm[H_A(2\lambda M_0 + H_A)]^{1/2}$ can have finite δm.

The extension to include k-dependent spin waves is direct and worth noting. For an example, consider the two-sublattice uniaxial antiferromagnet described by the following Hamiltonian:

$$\mathcal{3C} = -g\beta\{\sum_{\langle m(1), n(2)\rangle} K_{mn}\mathbf{S}_{m(1)}\cdot\mathbf{S}_{n(2)}$$

$$+ \sum_{\langle m(1), n(1)\rangle} J_{mn}\mathbf{S}_{m(1)}\cdot\mathbf{S}_{n(1)}$$

$$+ \sum_{\langle m(2), n(2)\rangle} J_{mn}\mathbf{S}_{m(2)}\cdot\mathbf{S}_{n(2)}$$

$$+ \sum_{\langle m(1)\rangle} H_A S_{m(1)}{}^z - \sum_{\langle m(2)\rangle} H_A S_{m(2)}{}^z\},$$
(9)

$m_{(i)}$ and $n_{(j)}$ are used as in Eq. (3), H_A is the anisotropy field, J is an intra- and K an intersublattice exchange field. Note that 1 is the up sublattice and J and K are positive (negative) for ferro- (antiferro-) magnetic coupling.

Leaving out perturbing fields, we have the following secular equations for the disturbances $\delta s_{m(i)}^+$:

$$\delta s_{m(1)}^+ = \chi^1(\omega)\{\sum_{n(1)} J_{mn}\delta s_{n(1)}^+ + \sum_{n(2)} K_{mn}\delta s_{n(2)}^+\},$$

$$\delta s_{m(2)}^+ = \chi^2(\omega)\{\sum_{n(2)} J_{mn}\delta s_{n(2)}^+ + \sum_{n(1)} K_{mn}\delta s_{n(1)}^+\}.$$
(10)

The χ^i are single-ion susceptibilities [see Eq. (5)]. If we denote the expectation value of the spins on 1, $\langle \bar{S}_1\rangle$ by S, we have

$$\chi^1(\omega) = \frac{S}{SJ(0) - SK(0) + H_A - \omega/\gamma},$$

$$\chi^2(\omega) = \frac{S}{SJ(0) - SK(0) + H_A + \omega/\gamma},$$
(11)

where $J(0)$ and $K(0)$ are defined below [Eq. (13)] as $k=0$ Fourier transforms of the "mn" quantities.

Now make the usual spin-wave substitution:

$$\delta s_{m(1)}^+ = \frac{1}{\sqrt{N}}\sum_k \delta s_1^+(k)e^{ik\cdot R_{m(i)}},$$
(12)

and similarly for the down spins. We define $J(k)$ and $K(k)$ as

$$J(k) = \sum_n J_{mn}e^{ik\cdot(R_n - R_m)},$$

$$K(k) = \sum_n K_{mn}e^{ik\cdot(R_n - R_m)}.$$
(13)

With some rearrangement, Eq. (10) becomes the following:

$$\delta s_1^+(k)\left\{\frac{1}{\chi^1(\omega)\chi^2(\omega)} - J(k)\left[\frac{1}{\chi^1(\omega)} + \frac{1}{\chi^2(\omega)}\right]\right.$$

$$\left. + J^2(k) - K^2(k)\right\} = 0.$$
(14)

The solution for the eigenfrequencies is

$$\omega/\gamma = \pm\{[SJ(0) - SK(0) - H_A$$
$$- SJ(k)]^2 - S^2K^2(k)\}^{1/2},$$
(15)

in agreement with the usual $T=0°K$ spin-wave result.[14] For $T \neq 0$, we may consider S and possibly H_A as temperature-dependent and arrive at the Tyablikov result.[15]

[14] L. R. Walker, in *Magnetism*, edited by G. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, p. 327.
[15] S. V. Tyablikov, *Methods in the Quantum Theory of Magnetism* (Plenum Press, Inc., New York, 1967), p. 250.

C. Equation-of-Motion–Quantum-Mechanical Hamiltonian

A simple Hamiltonian which displays the difference between the classical and quantum treatments is

$$\mathcal{3C}=D\sum_i (S_i{}^z)^2+J\sum_{\langle i,j\rangle} \mathbf{S}_i\cdot\mathbf{S}_j, \qquad (16)$$

where the sum $\langle i,j\rangle$ is over neighboring pairs. J is the exchange and D the crystal-field constants. The equation of motion for the operator $S_i{}^+$ is

$$\dot{S}_i{}^+= -i[S_i{}^+,\mathcal{3C}]=iD[S_i{}^z S_i{}^++S_i{}^+S_i{}^z]$$
$$+J\sum_{j,\text{neighbor}} [S_i{}^z S_j{}^+-S_j{}^z S_i{}^+]. \qquad (17a)$$

The classical limit [as in Eq. (1)] is achieved by replacing all operators by their expectation values. A better approximation is to take the expectation value of Eq. (17a) and ignore quantities like $\langle(O_i-\langle O_i\rangle)(O_j-\langle O_j\rangle)\rangle$ where $\langle\ \rangle$ means expectation value, O_i is some single-site operator, and i and j refer to *different* sites. This decorelation approximation may be called an RPA on different sites, or a time-dependent Hartee approximation. It is the only approximation involved in TDMF.

Equation (17a) now becomes

$$\langle\dot{S}_i{}^+\rangle=iD\langle S_i{}^+S_i{}^z+S_i{}^z S_i{}^+\rangle$$
$$+J\sum_{j,\text{neighbor}} [\langle S_i{}^z\rangle\langle S_j{}^+\rangle-\langle S_j{}^z\rangle\langle S_i{}^+\rangle]. \qquad (17b)$$

This is not equivalent to the classical Eq. (1) since it states that the development depends on more than specification of all $\langle S_i\rangle$; it depends on products of two operators as well. The next step then is to write equations for the double products. These involve triple products, always in operators referring to just one ion. The hierarchy of equations developed in this way is not endless; it is cut off when the single ion's level structure will support no higher products independent of those which came before.[16] The differential equations are then of sufficiently high order so that Fourier components related to all level splittings may be present in the solutions. The ultimate solution, proceeding via spin-wave spacial Fourier transforms for each $\langle O_i\rangle$, may seem difficult since equations of order number of transitions times number of sublattices must be solved. Still there are many situations for which a numerical solution is possible. Conceptually at least, there is no need to make further approximations such as decorrelation on the same site.[17]

There is a considerable lack of economy in the equation of motion method. First, we solve for a host of expectation values of products of operators. But, since the exchange has been assumed bilinear, the only quantities we really need are first order in the spin—it is only these which are needed when spins interact. Second, we deal with equations, some of which are ultimately related to weak transitions, not relevant to measurable effects. These points will become clear as we present the more economical formulation in Sub. II D. The difference in the following formalism is that it deals with equations for the density matrix rather than the operators and allows use to be made of compact single-ion susceptibilities.

D. Quantum Problem with Susceptilities

To present this point of view in a coherent fashion, we start again from the beginning. The problem is that of bilinear exchange coupling and arbitrary single-ion terms:

$$\mathcal{3C}=\sum_i (O_i-\mathbf{h}_i\cdot\mathbf{M}_i\cos\omega t)+\sum_{\langle i,j\rangle} \mathbf{S}_i\cdot\mathbf{J}_{ij}\cdot\mathbf{S}_j. \qquad (18)$$

O_i is a single-ion operator of i which contains crystal fields and interactions with static external fields, $\mathbf{M}_i$ is the magnetic moment and $\mathbf{S}_i$ the spin operators of i, $\mathbf{h}_i$ is the value of a small oscillating magnetic field at the site i, and the last term involving the sum over pairs $\langle i,j\rangle$ is the exchange interaction in tensor form.[18]

Equation (18) may be rewritten with no loss of generality:

$$\mathcal{3C}=\sum_i \left[O_i-\mathbf{h}_i\cdot\mathbf{M}_i\cos\omega t+\mathbf{S}_i\cdot\sum_j \mathbf{J}_{ij}\cdot\langle\mathbf{S}_j\rangle\right]$$
$$-\sum_{\langle i,j\rangle} \langle\mathbf{S}_i\rangle\cdot\mathbf{J}_{ij}\cdot\langle\mathbf{S}_j\rangle$$
$$+\sum_{\langle i,j\rangle} (\mathbf{S}_i-\langle\mathbf{S}_i\rangle)\cdot\mathbf{J}_{ij}\cdot(\mathbf{S}_j-\langle\mathbf{S}_j\rangle). \qquad (19)$$

One way of expressing the static (Weiss) molecular-field approximation is to say that the last term in (19) may be neglected providing a suitable set of numbers are chosen for $\langle\mathbf{S}_i\rangle$. As the notation anticipates, the most common choice is the self-consistent thermal expectation value. For TDMF, we take [as in Eq. (2)]

$$\langle\mathbf{S}_i\rangle=\langle\bar{\mathbf{S}}_i\rangle+\delta\mathbf{s}(t), \qquad (20)$$

where $\langle\bar{\mathbf{S}}_i\rangle$ is the static Weiss value and $\delta\mathbf{s}(t)$ is assumed small; that is, we assume a small response to small field $\mathbf{h}$. Then we rewrite $\mathcal{3C}$ again, leaving out the last term

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[16] This is the advantage of decoupling on sites. Equations for products of the Fourier transformed operators S_k are not so obviously limited.

[17] Decorrelation on the same site is usually done, however, in Green's-function work with single-ion terms [e.g., M. Tanaka and K. Tomita, Progr. Theoret. Phys. (Kyoto) **29**, 538 (1963); **29**, 651 (1963)]. A possible justification lies in the assumption regarding relaxation [H. Mori and K. Kawasaki, *ibid.* **27**, 529 (1962); K. Kawasaki and H. Mori, *ibid.* **28**, 690 (1962)]. It seems best to

avoid such approximations when single-ion terms are large and, as we see here, same-site decorrelation can be avoided.

[18] The magnetic moment operator M_i is L_i+2S_i or a suitable projection of it. The power of TDMF is displayed when O_i contains crystal-field terms like $S_z{}^2$ or $S_x{}^4 S_y{}^4$; these are handled just as easily as "anisotropy field" terms $H_a S_z$.

(and the constant) as is appropriate for our RPA:

$$\mathcal{3C} = \sum_i \left[\mathcal{3C}_{static}{}^i + \mathbf{h}_i \cdot \mathbf{M}_i \cos\omega t + \mathbf{S}_i \cdot \sum_j \mathbf{J}_{ij} \delta s_j(t) \right], \quad (21)$$

where

$$\mathcal{3C}_{static}{}^i = O_i + \mathbf{S}_i \cdot \sum_j \mathbf{J}_{ij} \langle \bar{\mathbf{S}}_j \rangle.$$

We have thus succeeded in dividing $\mathcal{3C}$ into a large static part (containing crystal field, Weiss molecular field, and static external field), and a small time-varying part. More importantly, $\mathcal{3C}$ is a sum of a single-ion Hamiltonians, coupled dynamically through the self-consistency requirements on the numerical expectation values, but nonetheless operating on distinct single-ion subspaces. This "kinematically" decoupled problem may be solved for small excitations in terms of the various frequency-dependent susceptibilities of the single ions, determined completely by $\mathcal{3C}_{static}$. It might be noted that in order to get $\mathcal{3C}_{static}$ we must solve the static self-consistent molecular-field problem. This is quite easy to do numerically to great accuracy.

For the general case where spin and magnetic moment are not simply related (as when orbital angular momentum is present), four kinds of susceptibilities are required. Their relation is illustrated for a two-ion system in Fig. 1.

The external field h' is generated by a coil; it acts on the spins via χ_{sh}, eliciting a response δs. Associated with the response is an exchange field (a TDMF) acting on spins via χ_{ss}. For a given h' and δs, we find δs [as in Eq. (6)] and ultimately express δs in terms of h' alone [as in Eq. (7)]. Now the external and exchange fields also elicit responses of the moment δm, this time via χ_{mh} and χ_{ms}, respectively. It is the moment which reacts with the coil yielding the final measurement of $\Xi_k{}^{(\omega)} = m_k/h_k$.

In the absence of relaxation, the χ's may be calculated from the energies and eigenstates of the static Hamiltonian by the Kramers-Heisenberg dispersion formula.[19] For example, the susceptibility of a (+) spin to a (+) magnetic field is given by

$$\chi_{sh}(\omega) = \sum_{a,b} \tfrac{1}{2}(\rho_a - \rho_b) \frac{S_{ab}{}^+ M_{ba}{}^-}{E_a - E_b + \hbar\omega + i\epsilon}, \quad (22)$$

where $S_{ab}{}^+$ and $M_{ba}{}^-$ are matrix elements between states a and b, E_a and E_b are eigenstate energies, and ρ_a is the Boltzman factor $\exp(-\beta E_a)/\mathrm{tr}\,\exp(-\beta\mathcal{3C}_{static}{}^i)$. The eigenstates and energies are those of $\mathcal{3C}_{static}{}^i$, the crystal and Weiss-molecular-field Hamiltonian.

[19] See, for example, D. ter Haar, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by D. ter Haar (Plenum Press, Inc., New York, 1961), p. 109. Other forms for χ [e.g., see R. Karplus and J. Schwinger, Phys. Rev. 73, 1020 (1948)] involve relaxation mechanisms and might be used in special cases where something about the relaxation is known.
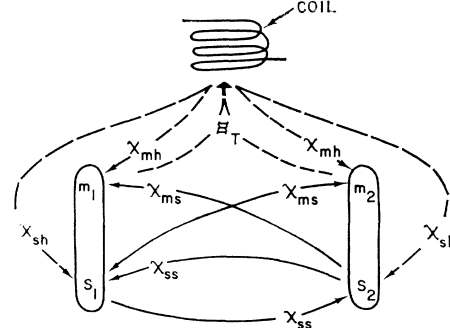

FIG. 1. Single-ion susceptibilities and the collective response. Interactions in an exchange coupled 2-spin system are shown. Solid lines are effective exchange fields (TDMF's), dashes are magnetic fields. Four kinds of single-ion susceptibilities (χ) are involved in giving the response of spin (S) and magnetic moment (m) to exchange and magnetic fields. The coupled response equations (ω-Fourier transformed and taking some liberty with units) are $\delta s_1 = \chi_{ss} J \delta s_2 + \chi_{sh} h$, $\delta s_2 = \chi_{ss} J \delta s_1 + \chi_{sh} h$. These are solved for δs_1 and δs_2 as linear responses to h alone. The relations for δs are substituted in the following: $\delta m_1 = \chi_{ms} J \delta s_2 + \chi_{mh} h$, $\delta m_2 = \chi_{ms} J \delta s_1 + \chi_{mh} h$, to get $\delta m_1 + \delta m_2$ as a linear response to h. The collective susceptibility Ξ, the ratio of $\delta m_1 + \delta m_2$ to h, is quite different from the underlying χ's.

The solution for the moment response looks like

$$\delta m_i = \chi_{mh}{}^{(\omega)} h_i e^{-i\omega t} + \chi_{ms}(\omega) \sum_j J_{ij} \cdot \delta s_j, \quad (23)$$

where δs_j can be expressed in terms of $\delta s(k)$, the Fourier transform derived from an equation like Eq. (14) with forcing terms proportional to h_k, the Fourier-transformed external field, on the right-hand side. Since all quantities on the right-hand side of Eq. (23) are then expressed in terms of h_i, all the δm_i and their transforms δm_k are similarly expressible for any given frequency (ω) and wave vector ($\mathbf{k}$) of the perturbing field. The poles of $\Xi_k(\omega) = \delta m_k(\omega)/h_k$ give the positions, and the residues the strengths of the moments of normal modes. Since the denominators in the χ's [see Eq. (22)] involve, in general, many frequency differences, there are many normal mode solutions, especially at high temperatures where transitions among excited states may contribute. However, the modes are never the same as the underlying single-ion transitions, although the weaker and more separated of them do appear substantially unaltered. Modes bearing little resemblance to any single-ion transition also occur. The total susceptibility $\Xi_k(\omega)$ contains all information about magnetic normal modes as well as all magnetic dipole effects in resonance, optical absorption, and neutron diffraction.

Where there is a twofold axis, it is possible to identify transverse or π-active modes and longitudinal or σ-active modes. When there is no symmetry, all modes mix. Even in this "worst" case, sets of simultaneous equations of order no higher than three times the number of sublattices must be solved for each k and ω. Many values of ω must be examined to find the poles, so
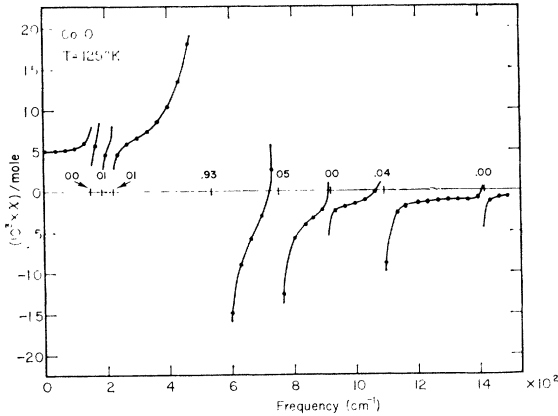
Fig. 2. Transverse magnetic susceptibility (real part) for uniform field at various frequencies in the CoO model at 125°K. Dots are computed points at 30-cm⁻¹ intervals, and the curves represent a finer plot in regions near the poles. The residue at each pole is given in cm⁻¹/mole to the nearest hundredth. The value of $\chi(0)$ for this model agrees with static measurements—other predictions here are unchecked. The model Hamiltonian spans the lowest L triplet and S quartet and has an L_z^2 anisotropy term plus spin-orbit coupling [M. Tachiki, J. Phys. Soc. Japan **19**, 454 (1964)].

the computation may be considerable, but in most cases this situation is preferable to dealing with one much larger system of equations as in the equation-of-motion formalism (Sec. II C).

In the "best" case, where symmetry permits a division of modes into left and right transverse and longitudinal, TDMF proceeds very rapidly—even when there are many allowed transitions.

Figure 2 shows the transverse susceptibility, $\Xi(\omega)$, $\mathbf{k}=0$ of a model representing the lowest 12 states of Co²⁺ in CoO at 125°K. There are several weak poles which do not show clearly on this scale, but it is to be remembered that exceedingly weak transitions will not be observed in any case. Thus, a certain economy is achieved in that, if desired, only large transitions in a specified range of ω need be investigated. Important poles, and their residues as determined from a fine scale plot are indicated on the figure.

III. EXAMPLES

Aspects of TDMF are illustrated in the following six examples. The version of TDMF is one where relaxation is left out; the susceptibilities are computed from the Kramers-Heisenberg formula. The widths of the lines in illustrations are simply chosen so that the relative intensities (proportional to area) can be well displayed.

A. Equal-Spaced n-Level System

The first example shows the relation of TDMF to linear spin-wave theory. Consider the following Hamiltonian:

$$\mathfrak{IC}=\sum_i \mathbf{H}_i^{\mathrm{eff}}\cdot\mathbf{S}_i^+ \sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{J}_{ij}\cdot\mathbf{S}_j, \qquad (24)$$

H_i^{eff} is some numerical effective field acting on the ith ion, it might be representing anisotropy and perhaps be temperature-dependent.[20] [For other symbols see Eq. (18).] The static molecular-field configuration need not be collinear; external fields are included in $\mathbf{H}_i^{\mathrm{eff}}$. For any given ion, it is clear that the energy levels of $\mathfrak{IC}_{\mathrm{static}}$ are equally spaced.

The equal-spaced system has the special property that the equations of motion for the transverse components of $\mathbf{S}_i$ involve no higher-order products on the same site, so the equation of motion or TDMF formalisms are equally convenient. The results are equivalent. There is just one single-ion frequency associated with allowed transitions on each sublattice; the coupled system also has as many modes as sublattices.

Now, theories which produce linear equations are equivalent to forming models like Eq. (24). Thus, linearized spin-wave theory which applies RPA-type decoupling on the same site, as well as the more sophisticated approach of Kanamori and Tachiki,[21] are nothing more than ways of reducing a complicated system to an equally spaced one. The number of normal modes in the equally spaced system is quite limited.

B. Three-Level System

This example illustrates the relation of the TDMF to the underlying single-ion transitions. Consider a two-sublattice antiferromagnet of spin one described by the Hamiltonian

$$\mathfrak{IC}=-\sum_k D[S_k^z]^2+J\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j, \qquad (25)$$

where i runs on the up and j on the down sublattice, and J is the (intersublattice) exchange, taken here as 30 cm⁻¹; k runs over all sites; D is taken as 10 cm⁻¹. We examine uniform modes in a transverse perturbing field. There are no longitudinal modes since m_z is a good quantum number.
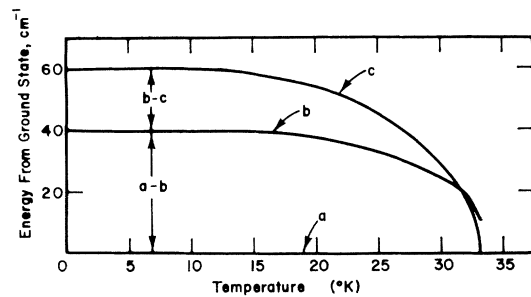

Fig. 3. Single-ion transition energies for three-level model as a function of temperature. The height of c level is a direct measure of the exchange field.

[20] Physical reasoning requires temperature-dependent coefficients when anisotropy is represented by an effective field. For realistic forms of crystal-field terms (to be considered later) the basic temperature dependence follows naturally.

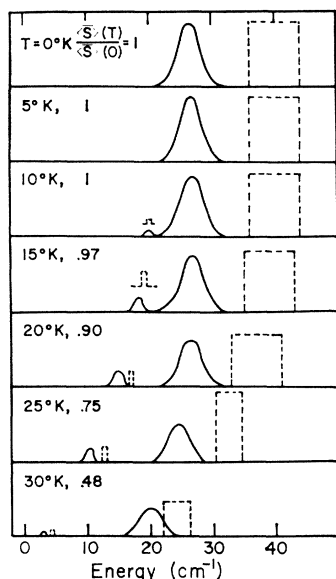[21] J. Kanamori and M. Tachiki, J. Phys. Soc. Japan **17**, 1384 (1962).

Fig. 4. Absorptions in three-level model at seven temperatures. Single-ion transitions are given by dotted rectangles, actual predictions for the coupled system by continuous lines. The temperature and corresponding value of $\langle \tilde{S} \rangle (T)/\langle \tilde{S} \rangle (0)$, the normalized z-spin expectation value, are given on the left. Linewidth is not included in this calculation—the shapes in the figure are chosen to conveniently display intensity (proportional to area). The intensity for the $T=0°K$ line corresponds to 1300 cm^{-2}/mole cm^3.

Figure 3 shows the energy levels as a function of temperature. There are two allowed single-ion transitions, a-b and b-c. If the neighbors of a given ion are clamped in their Weiss field positions, these two "single-ion" lines would be observed with characteristic single-ion intensities. In TDMF, the effect of precessing neighbors pulls the two modes and alters the intensities. a-b become the antiferromagnetic resonance (AFMR) line with intensity considerably less than the pure magnetic dipole intensity which characterizes the single-ion line. b-c is not present at $T=0$. For high temperatures, b-c is shifted only slightly, since it is weak. TDMF solutions for seven temperatures are shown in Fig. 4, along with the invisible underlying "single-ion" transitions.

The effect of temperature is twofold. The level structure changes as the exchange field decreases. Also, upper states populate lowering terms in the (single-ion) χ's associated with ground-state transitions and raising excited state contributions. The result is usually a net decrease in the effective anisotropy; the strongest modes tend to fall in frequency. The drop accords with the usual approximation[22] when exchange dominates. However, if a high-temperature line appears near the main mode, they repel and the strong mode may actually rise with temperature. This may be interpreted in terms of a stiffening above a resonance.

[22] C. Zener, Phys. Rev. 96, 1335 (1954); H. B. Callen and E. Callen, J. Phys. Chem. Solids 27, 1271 (1966).

Near the (molecular-field) Néel point, the static exchange field drops and the ± 1 states coalesce. Even in the paramagnetic regime, however, the $j=0$ state remains separated and in both the single-ion and TDMF pictures a single nonzero mode of considerable intensity remains.

C. Orthorhombic Four-Level System

The next example is richer in detail. The significant features demonstrated are (i) the lines associated with excited state transitions can be very strong while the spin is still close to its $T=0°$ value; (ii) σ-active modes exist and can be quite strong[23]; (iii) TDMF modes occur only in the frequency region where there are single-ion transitions, but they do not necessarily reflect them closely.

The Hamiltonian for this orthorhombic four-level model with two antiferromagnetic sublattices is

$$\mathcal{H}=\sum_k \left[-DS_k^{z2}+E(S_k^{x2}-S_k^{y2})\right]+\sum_{\langle i,j \rangle} J_1 \mathbf{S}_i \cdot \mathbf{S}_j$$
$$+\sum_{\langle i,i' \rangle} J_2 \mathbf{S}_{i'} \cdot \mathbf{S}_i + \sum_{\langle j,j' \rangle} J_2 \mathbf{S}_{j'} \cdot \mathbf{S}_j, \quad (20)$$

where k runs over both sublattices, i and i' over the up and j and j' over the down sublattice neighbors. J_1, the interexchange, is 40 cm^{-1}, J_2 (intra) is 20 cm^{-1}, E is 10 cm^{-1}, and D is 15 cm^{-1}.
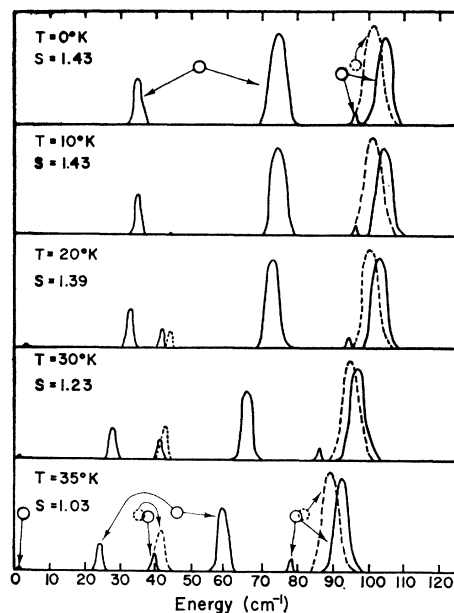

Fig. 5. Absorptions in the four-level orthorhomic model. π-active transitions are shown by the solid line, σ transitions by the dashed lines. The circles given on the $T=0$ and 35°K plots show the location of the underlying single-ion transitions and the lines to which they are most closely associated. Width is chosen for convenience. The intensity of the $T=0°K$ σ-active line is 3300 cm^{-2}/mole cm^3.

[23] σ-active modes are quite awkward to represent in linear spin-wave theory.
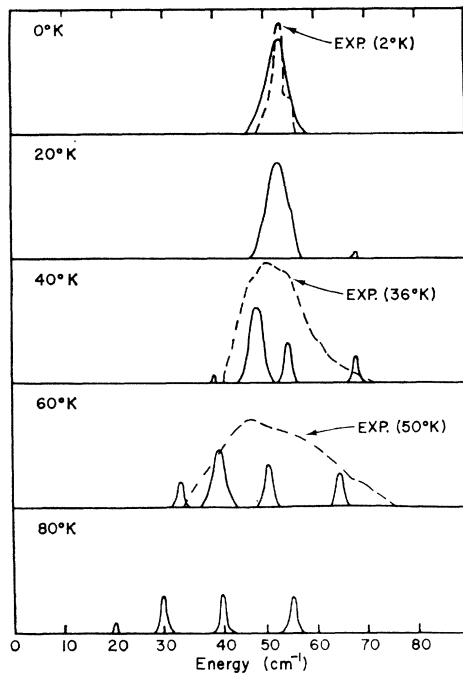
FIG. 6. Absorptions for the five-level model for FeF$_2$. As before, only area and line position are of significance for the predictions (solid curves). The intensity shown for the $T=0°$K predicted line is 220 cm^{-2}, the same as that given by spin-wave theory. A rough summary of the data of Ohlmann and Tinkham is shown for three temperatures. No close comparison is intended, the only point being that the predicted multiple lines could be hidden in the broadened experimental results.

Because of the twofold axis about z, we may distinguish eliptical, nondegenerate π modes and σ modes. The σ modes arise because S_z couples nondegenerate states. The predicted lines are given in Fig. 5 for five temperatures. As before, intensities are proportional to area, the width chosen, so that all lines have the same shape. The incident light is assumed circular for the π modes and linear for the σ. Only half of the possible σ modes are visible at zero external field; the out-of-phase oscillations have no moment. For nonzero temperatures we see two of four σ, and six of eight π lines. The omitted π lines are too weak to be displayed. The molecular-field Néel point for this model is 45°K. Note that the position of the six doubly degenerate single-ion transitions and their relation to cooperative modes is indicated for $T=0$ and 35°K.

D. Five-Level FeF$_2$ Model; Spin-Wave Dispersion

The next example is the five-level $(S=2)$ system specified by

$$\mathcal{H}=\sum_k -D[S_k{}^z]^2+J\sum_{\langle i,j\rangle} \mathbf{S}_i\cdot\mathbf{S}_j. \qquad (27)$$

D is 6.5 cm^{-1} and J_1, an intersublattice exchange, is 30.8 cm^{-1}. The form and parametrization of (27) is

suggested by Ohlmann and Tinkham, and Lines to represent Fe^{2+} ions in FeF$_2$.[24]

The system is axially symmetric; there are no σ modes. At $T\neq0°$K, there are four allowed π modes, doubly degenerate in zero field. The predictions are given in Fig. 6. On this figure, the experimental results at three temperatures are included. The points to be made are as follows: (i) The exact fit at $T=0°$K is because here there is only one contributing transition. With only one transition TDMF is equivalent to linear equation-of-motion results. Since the parameters were chosen to fit the AFMR as derived from the spin-wave linear equations,[24] the agreement is inevitable. (ii) For $T\neq0°$K, the experimental results show marked broadening; there is a possibility of unresolved multiple lines predicted by TDMF. No claim to close agreement is made. (iii) The TDMF and static molecular-field theory share the same high-temperature limitations. For example, in Fig. 6 predictions are included for 80°K, a temperature below the self-consistent molecular-field Néel point for the model, but higher than T_N for FeF$_2$. Significance can be extracted from results in this region only with great care. One way out is to set the exchange such that agreement for the Néel point is achieved—this is rejected. Molecular-field theory is least accurate in the critical region; it is pointless to choose wrong parameters to force the theory near T_N. Exchange is
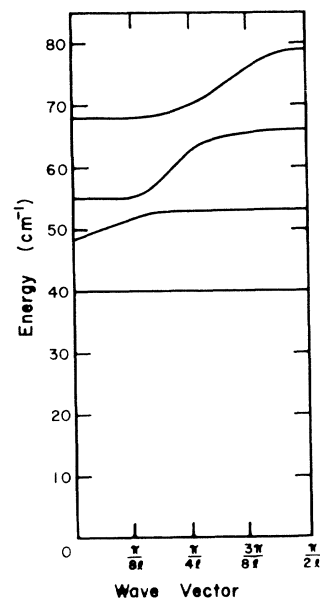

FIG. 7. Energy dispersion for x direction in FeF$_2$, model at 30°K. Each of the four lines has some k dependence. Note how the line which starts at 48 cm^{-1} crosses those above it. l is a characteristic dimension for the FeF$_2$ structure. $\pi/2l$ is half way to the first zone face.

[24] R. C. Ohlmann and M. Tinkham, Phys. Rev. **123**, 425 (1961); M. E. Lines, *ibid.* **156**, 543 (1967).

best set from more reliable measurements.[25] Another way is to plot versus T/T_N or against $\langle S \rangle$. There is no rigorous justification for scaling. A third possibility is to sacrifice the self-consistency requirement on $\langle S \rangle$ and insert experimental values. The disparity between actual and molecular-field sublattice moments is in any case small to a large fraction for T_N for systems with large anisotropy.[26] The ultimate temperature range of usefulness of TDMF is not clear at this time.

An example of the dispersion for spin-wave-like excitations is presented in Fig. 7. Here, are given the energies as a function of k vector along $(1,0,0)$ for the FeF_2 model at 40°K. There are four bands. The strongest line is usually most sensitive to changes in k. Here, it crosses the two slower changing modes above it.[27]

E. Three-Level System with External Field

This model is same as Eq. (25) (Ex. 2) except that a magnetic field, along $\hat{x}$,[28] is added. Results are summarized in Fig. 8. The energies are plotted versus H^2 for the lines at 20°K. Numbers above each line give the
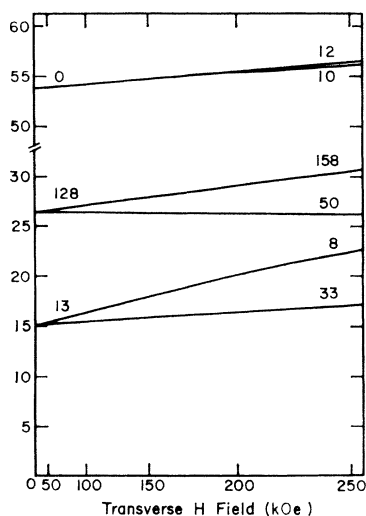

FIG. 8. Absorption energies as a function of transverse magnetic field in the three-level model at 20°K. The ordinate is in cm^{-1}. For zero field there are two π-active lines. These split and change in energy approximately as the square of the field H_x. Also, at high field, a third transition becomes allowed. The angle of canting of the spin axis from z is 4.3° at 50 kOe, 24.3° at 250 kOe. The relative intensities to right circularly polarized light is given above each line for zero field and for 250 kOe.

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[25] For the particular case FeF_2, it has been suggested (M. E. Lines, above) that better agreement for the molecular-field theory T_N could be obtained from a better choice of parameters, including next-nearest-neighbor exchange. In any event, the point is that molecular-field values for T_N are not expected to be as accurate measures of J's as $T=0$°K dynamic experiments, for example.

[26] See M. E. Lines, Phys. Rev. **156**, 534 (1967).

[27] We plot to only half the zone edge as there is a double periodicity in this example. The reason is a symmetry discussed by K. Kawasaki, Phys. Rev. **142**, 164 (1966).

[28] Any field direction could be used. z would be easiest, but x is more interesting.
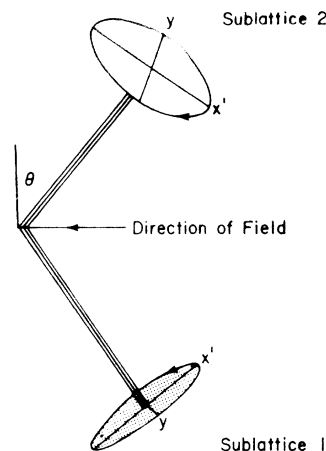

FIG. 9. The normal modes for the three-level model at 20°K in 250 kOe transverse field. The motion is conveniently represented as an eliptical precession in a plane for each sublattice. θ specifies the angle that the normal to each plane makes with the z axis. Values of tanθ and the in-plane sublattice motion are listed below for the modes at 250 kOe.

Frequency (cm^{-1})	Tanθ	Motion of sublattices x'	y
17.25	0.54	$\cos\omega t$	$-2.76 \sin\omega t$
22.30	0.72	$1.80 \cos\omega t$	$- \sin\omega t$
26.19	0.26	$\cos\omega t$	$-2.23 \sin\omega t$
30.72	0.40	$2.04 \cos\omega t$	$- \sin\omega t$
56.48	0.09	$\cos\omega t$	$-1.67 \sin\omega t$
56.48+	0.24	$1.76 \cos\omega t$	$- \sin\omega t$

Note that if the motion preserved the length of the spin vector to first order in small quantities, then the plane of precession would be perpendicular to the static spin direction. In that case, tanθ would be 0.41.

intensities to π-polarized light for 0 field and 250 kOe for each mode. In Fig. 9, we present a description of the spin precession involved in each of the six modes in 250-kOe applied field. Note that the precession does not preserve the length of the spin expectation value, even to first order.

We might note that the TDMF procedure when external fields are present is unaltered from before. The field is included in $\mathcal{H}_{\text{static}}$ and reflects in the self-consistent $\langle S \rangle$'s as well as the level structure and the X's. Dependence of effective anisotropy on sublattice angle, canting of sublattices with field, unquenching of orbital angular momentum, etc., are included automatically.

IV. COMMENTS

A strength of TDMF in applications is its generality. The modifications between treating different systems are very slight; it is easy to automate the procedure. In our work, the model Hamiltonian and relevant spin and moment operators are entered as numerical matrices and the sublattice configuration and couplings are specified. The rest of the procedure is invarient from system to system.

Both a strength and weakness is that fact that TDMF is a "first-principles" theory, i.e., it starts from a Hamiltonian. If the Hamiltonian can be parametrized, such a theory is clearly good, but it usually takes many data before an unequivocal parametrization is possible. When there are not many data, phenomenological concepts, such as "anisotropy fields," may provide as good a description as warranted; complicated theories add nothing. Even so, since TDMF is a physical approximation, the relation of underlying parameters to results is almost always transparent. Where the Hamiltonian is of simple form, it is hard to see why any less complete a description should be settled for.

Before concluding it should be mentioned that the TDMF procedure bears some relation to what has been called an excitation wave approach. That approach, which is also applicable to complicated Hamiltonians in an RPA, has been developed and used by Trammel,[29] Van Vleck,[30] and others[31] in discussing rare-earth ions. The method consists of identifying the excitations from the molecular-field ground state of a given ion with the first excitations of a set of harmonic oscillators. It is of interest that in the limit of zero temperature, the results of this method for both normal mode frequencies and moments, are identical to those of TDMF for a large class of problems. That this is so follows by considering the equations of motion of each boson operator and noting that an operator of one ion couples only to the combinations of boson operators from other ions which constitute the transcribed spin operators.[32] The ex-

tension of the excitation wave method to high temperature has apparently not been done.

One reason to prefer TDMF is that it is applicable, formally at least, at all temperatures including the paramagnetic region.[33] Another advantage is that it involves only spins and magnetizations and thus far fewer and more physical unknowns, especially when the number of allowed excitations is large.

In conclusion, we have described the TDMF method of doing magnetic excitations. It includes various effects related to detailed ion dynamics as well as conventional spin waves. Its advantages are most obvious in cases where anisotropy is large compared with exchange, and where orbital angular momentum is important.

ACKNOWLEDGMENTS

[29] G. T. Trammell, J. Appl. Phys. **31**, 3625 (1960).
[30] R. M. Bozorth and J. H. Van Vleck, Phys. Rev. **118**, 1493 (1960).
[31] B. Grover, Phys. Rev. **140**, A1944 (1965); B. R. Cooper, *ibid.* **163**, 444 (1967).
[32] The reader will recall that in the excitation wave approach, a set of Bose operators are written to represent the excitations from the ground state to excited states of the single ion. Then, substitutions are made for the various operators according to the prescription

$$S \rightarrow a_e^\dagger \langle e|S|g\rangle + a_e \langle g|S|e\rangle + a_e^\dagger a_e [\langle e|S|e\rangle - \langle g|S|g\rangle],$$

where e refers to excited states and g is the ground state. Somewhat symbolically and assuming a bit of symmetry, the equation of

motion for a typical destruction operator might be

$$\hbar \omega a_e^1 = (E_1g - E_1e)a_e^1 + J\langle e_1|S_1|g_1\rangle S_2,$$

where a_e^1 relates to ion No. 1, and S_2 is the spin of ion No. 2 before it is decomposed by the prescription above. E_1g and E_1e are ground- and excited-state energies, respectively. Now multiply each a_e by $\langle g|S|e\rangle$ and sum on excited states. Reconstituting S_1, we get

$$S_1 = J\sum_e |\langle e_1|S_1|g_1\rangle|^2/(E_1g - E_1e - \hbar\omega)S_2,$$

which is then just like Eq. (23) for χ evaluated $T=0°K$ and with no external exciting field.

[33] TDMF accounts for spin-wave interactions by changing the average level propulations. This is clearly a crude approximation, cruder in fact, than the principle of the usual spin-wave RPA. Results for states with large fluctuations (high temperature) are thus of limited accuracy. On the other hand, errors are limited to the magnitude of exchange effects so single-ion-like lines, dominated by crystal-field effects, are all right in any state, paramagnetic as well as ordered. (Of course, for them the completely decoupled single-ion theory should be satisfactory.) A general statement as to how well and for which lines the TDMF RPA captures the average effect of thermal spin waves awaits comparison with experiment.
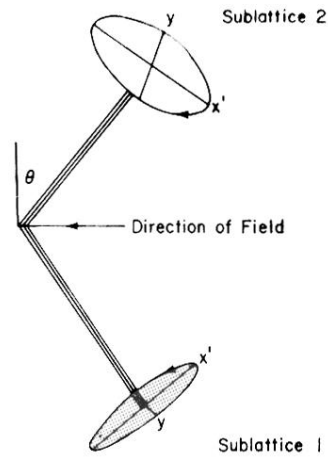
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