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Green's-Function Theory of an Induced Moment System Containing Impurities: Paramagnetic Phase*

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An induced moment system containing a substitutional impurity is studied using the Green's-function method in the random phase approximation. All the ions are assumed to have a singlet crystal field ground state and a singlet excited state. We focus our attention on the paramagnetic phase, without local polarization, in this paper. Two s-type modes are predicted in a lattice with only nearest-neighbor exchange interactions. The energies of the impurity modes have been calculated as functions of the impurity parameters and the temperature for a simple-cubic lattice. Similar to an ordinary impure magnetic system, local modes can appear above the energy band of the host and/or in the energy gap. The spectral weight function at the impurity site is discussed. Local susceptibilities, which are proportional to the temperature-dependent part of the NMR Knight shift, are calculated and compared with predictions of the molecular-field theory. The experimental situation is also reviewed.

I. INTRODUCTION

The problem of the effects of impurities in magnetic spin systems has been an active field of study in recent years. In particular, the localized excitations, the magnetization at the impurities, and the effects of impurities on the spin-wave spectrum of the host crystal are the central topics of discussions for impure magnetic insulators.[1-3] They are of interest both theoretically and experimentally, as the measurements of these quantities provide valuable information on the interactions of the impurity ions with the host ions. In this paper, we examine an induced moment system containing a substitutional impurity. Along with the behavior similar to an impure ordinary spin system, we also note the interesting features unique to the impure induced moment systems.

Induced moment systems with a singlet crystal-field ground state have been discussed by Trammel[4] and Bleaney[5] in the molecular-field approximation, and by Wang and Cooper[6] using a Green's-function method. It was shown that for rare-earth compounds with a singlet crystal field ground state for the rare-earth ions, the exchange interaction between neighboring ions must exceed a certain critical value relative to the crystal field to have magnetic ordering even at zero temperature. The magnetic moment which then occurs is essentially an induced moment corresponding to the Van Vleck susceptibility, where the exchange field takes the place of an applied magnetic field. When the exchange is less than the critical value the system is paramagnetic, as is a system with larger exchange above its critical temperature. Collective spin-wave-like exciton modes have been predicted in the ordered phase as well as in the paramagnetic phase.[4,6-8] Indeed, a large dispersion in the exciton energies in the paramagnetic phase has been observed recently by neutron inelastic scattering on praseodymium single crystals.[9]

In this calculation we consider an impure induced moment system in the paramagnetic phase. This requires not only that the pure host be a paramagnet, but also that the impurity be either a nonmagnetic ion or an ion with a nonmagnetic crystal field ground state. For the latter case we also assume that the local self-polarization centered at the impurity does not occur.[10] Localized excitations and local susceptibilites are of special interest as they are accessible to experimental measurements. Neutron inelastic scattering[3] and Raman scattering[11] are the well-known techniques used to probe the localized excitations of an impure system. Specific-heat measurement can also be a possibility, especially when the localized modes occur in the energy gap (as will be discussed later). To measure local susceptibilities, NMR or Mössbauer techniques can be used.

A method of thermal Green's functions is employed for the theoretical calculation. To simplify the algebra, we assume that each ion can be represented by a two energy-level system. That is, in the crystal field, each ion has a singlet ground state and a singlet first excited state; all other energy levels have much higher energies and can be neglected in our discussion. The pseudospin formalism of Wang and Cooper[8] is used and the Green's functions of interest are calculated in the random phase approximation. The explicit results are presented for a simple-cubic crystal with exchange interactions only between an ion and its nearest neighbors. These simplifications will obviously not allow a detailed study of the real crystals but the qualitative features of the problem will not be greatly affected. Only a single impurity is considered; this is a good approximation when the impurity concentration is small and the impurities are largely isolated from each other. Finally, we require that the thermal average of the z component of pseudospin $\langle S_j^z \rangle$, which measures the population of elementary excitations at a given site j, differs from the pure-crystal value only at the impurity site. That the perturbation due to the impurity ion is localized has been discussed by many authors.[2] This approximation enables us to solve for the Green's functions within the small cluster consisting of the impurity ion and its nearest-neighbor host ions.

With these assumptions we find that the only possible impurity modes are of s type, and they may appear above the host energy band and/or in the gap, depending on the impurity-host exchange-coupling strength and the impurity crystal field energy-level splitting. The energy of the local mode is calculated as a function of the impurity parameters and temperature. This local-mode energy greatly affects the population of excitations at the impurity site and therefore the susceptibility of the impurity ion. The temperature dependence of the local susceptibility of the impurity in the present Green's-function theory is then compared with the molecular-field calculation. In Sec. II we formulate the Green's-function theory for the two-level induced moment system containing a single impurity which can also be represented by two energy levels. The localized impurity modes are discussed in Sec. III. Section IV contains the numerical results for the energies of the local modes and the local susceptibility at the impurity site. A discussion of the experimental situation is also included. Numerical calculations of the pure-crystal Green's functions are described in the Appendix.

II. GREEN'S-FUNCTION FORMALISM

The Hamiltonian for the induced moment system containing a single impurity at the origin of the coordinates, with only nearest-neighbor exchange coupling between magnetic ions, can be written

$$H=\sum_l V_{cl} - \mathcal{J}\sum_l \sum_\delta \vec{J}_l \cdot \vec{J}_{l+\delta} - 2(\mathcal{J}_0 - \mathcal{J})\sum_\delta \vec{J}_0 \cdot \vec{J}_\delta \;, \qquad (2.1)$$

where V_{cl} is the single-ion crystal field potential at site l, which gives a singlet ground state and a singlet excited state separated by an energy gap Δ for the host ions and an energy gap Δ_0 for the impurity ion. As the impurity is introduced into the lattice to substitute for a host ion, we assume that the crystal field is not affected appreciably even for the host ions around the impurity. $\mathcal{J}$ and $\mathcal{J}_0$ are, respectively, the host-host and host-impurity exchange-coupling parameters. $\vec{J}_l$ is the total angular momentum of the ion at site l and $\vec{\delta}$ represents a vector directed from an ion to one of its nearest neighbors.

As discussed in Ref. 10, local self-polarization can occur as the impurity (even if it is an ion with singlet crystal field ground state) is added to a paramagnetic host crystal. To recapitulate the results, let $|0_{cl}\rangle$ and $|1_{cl}\rangle$ be the two singlet crystal field energy states for the ion at site l. In the presence of exchange interaction, the molecular-field eigenstates for ion l can be written

$$|0_l\rangle = \cos\theta_l |0_{cl}\rangle + \sin\theta_l |1_{cl}\rangle \;, \qquad (2.2a)$$

$$|1_l\rangle = -\sin\theta_l |0_{cl}\rangle + \cos\theta_l |1_{cl}\rangle \;, \qquad (2.2b)$$

where

$$\tan 2\theta_l = \frac{A}{z\alpha}\left[\sum_\delta J_{l+\delta} + \left(\frac{\mathcal{J}_0}{\mathcal{J}} - 1\right) J_0 \sum_\delta \Delta_{l,\delta}\right] \quad \text{for } l \neq 0 \;, \qquad (2.3a)$$

$$\tan 2\theta_0 = \frac{A_0}{z\alpha_0}\sum_\delta J_\delta \;. \qquad (2.3b)$$

Here we have defined $A \equiv 4\mathcal{J} z\alpha^2/\Delta$ and $A_0 = 4\mathcal{J}_0 z\alpha_0^2/\Delta_0$, where z is the number of nearest neighbors of an ion, and α and α_0 are the matrix elements of J^z between the crystal field ground state and excited state for the host ions and the impurity ion, respectively. J_l denotes the thermal-averaged value of the z component of the total angular momentum $\vec{J}_l$, and $\Delta_{l,\delta}$ is the Kronecker δ function. The J_l in Eqs. (2.3) are to be determined self-consistently. At zero temperature,

$$J_l = \langle 0_l | J_l^z | 0_l \rangle = \alpha_l \sin 2\theta_l \;. \qquad (2.4)$$

Combining Eqs. (2.3) and (2.4), we obtain

$$J_0 = \frac{1}{z} A_0 \left(\sum_\delta J_\delta\right)\left[1 + \left(\frac{1}{z} A_0 \sum_\delta \frac{J_\delta}{\alpha_0}\right)^2\right]^{-1/2} , \qquad (2.5a)$$

$$J_\delta = \left(\frac{1}{z} A \sum_{\delta'} J_{\delta+\delta'} + \frac{\mathcal{J}_0}{\mathcal{J}} \frac{A}{z} J_0\right) \times \left[1 + \left(\frac{1}{z} A \sum_{\delta'} \frac{J_{\delta+\delta'}}{\alpha} + \frac{\mathcal{J}_0}{\mathcal{J}} \frac{A}{z} \frac{J_0}{\alpha}\right)^2\right]^{-1/2} ,$$

$$\delta + \delta' \neq 0 \qquad (2.5b)$$

$$J_l = \frac{1}{z} A \Big(\sum_\delta J_{l+\delta}\Big)\left[1 + \left(\frac{1}{z} A \sum_\delta \frac{J_{l+\delta}}{\alpha}\right)^2\right]^{-1/2} \quad (\text{for } l \neq 0,\ \delta)\,. \tag{2.5c}$$

For our case of interest, the pure-host crystal is an induced moment paramagnet. Thus we take $A < 1$ and there is no long-range magnetic ordering.[5] The local self-polarization can occur, however, and the criterion for its occurrence must be considered. This has been presented in Ref. 10, where a classical Green's-function method similar to that used in the impurity problem of a harmonic lattice[12,13] was adopted to solve the Eqs. (2.5) near the critical point at which the local self-polarization vanishes. The criterion for the local self-polarization is, in molecular-field theory,[10]

$$A_0 = (\mathcal{J}/\mathcal{J}_0)\, A/(1 - [G_A(0)]^{-1})\,, \tag{2.6}$$

where

$$G_A(0) = \frac{1}{N} \sum_{\vec{k}} (1 - A\gamma_{\vec{k}})^{-1}\,. \tag{2.7}$$

Here the summation is over the first Brillouin zone of the lattice; N is the total number of atoms in the crystal, and $\gamma_{\vec{k}}$ is defined in the usual way, $\gamma_{\vec{k}} \equiv (1/z)\sum_\delta e^{i\vec{k}\cdot\vec{\delta}}$. Equation (2.6) can be rewritten in another form, which displays the impurity parameters of the system,

$$\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\right)^2 = \frac{\Delta_0}{\Delta}\, \frac{1}{1 - [G_A(0)]^{-1}}\,. \tag{2.8}$$

For the finite-temperature case, we need only to redefine A and A_0 in Eq. (2.6) as

$$A = (4\mathcal{J}z\alpha^2/\Delta)\tanh(\Delta/2k_BT)$$

and

$$A_0 = (4\mathcal{J}_0 z\alpha_0^2/\Delta_0)\tanh(\Delta_0/2k_BT)\,.$$

Equation (2.8) then becomes

$$\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\right)^2 = \frac{\Delta_0}{\Delta}\, \frac{\tanh(\Delta/2k_BT)}{\tanh(\Delta_0/2k_BT)}\, \frac{1}{1 - [G(0)]^{-1}}\,. \tag{2.9}$$

Here $G_A(0)$ is evaluated at

$$A = (4\mathcal{J}z\alpha^2/\Delta)\tanh(\Delta/2k_BT)\,.$$

A plot of $(\mathcal{J}_0\alpha_0/\mathcal{J}\alpha)^2$ vs Δ_0/Δ for various values of A is shown in Fig. 1 for a simple-cubic lattice at $T=0$. The same figure can also be regarded as a plot of $(\mathcal{J}_0\alpha_0/\mathcal{J}\alpha)$ vs $[\Delta_0\tanh(\Delta/2k_BT)]/[\Delta\tanh(\Delta_0/2k_BT)]$ for finite T. This then enables one to find the critical temperature at which the local self-polarization vanishes. It should be noted that Eq. (2.9) can be easily generalized to account for cases where the excited state is a multiplet instead of a singlet. A more accurate criterion taking into account the excitation waves in the system can be obtained as the condition for the vanishing of the energy of a local mode (calculated later). This changes Eq. (2.9) by replacing the ratio of the population factors, $\tanh(\Delta/2k_BT)/\tanh(\Delta_0/2k_BT)$, by the corresponding Green's-function result. To ensure that the local self-polarization does not occur we choose the ratio of $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ to be less than the critical ratio for a given Δ_0/Δ ratio and parameter A of the host crystal.

Following Wang and Cooper[6] we introduce the pseudospin $S=\frac{1}{2}$ for each ion. We assign $S^z=\frac{1}{2}$ to the molecular-field ground state (the crystal field ground singlet here) and $S^z=-\frac{1}{2}$ to the excited state. The Hamiltonian, Eq. (2.1), in the pseudospin variables is then

$$H = -\Delta\sum_l S_l^z + (\Delta_0 - \Delta)S_0^z - 4\mathcal{J}\alpha^2\sum_l\sum_\delta S_l^x S_{l-\delta}^x - 8\alpha(\mathcal{J}_0\alpha_0 - \mathcal{J}\alpha)S_0^x\sum_\delta S_\delta^x\,. \tag{2.10}$$

We consider the following Green's functions[14]:

$$G_{il}^+(t) = -i\theta(t)\langle[S_i^+(t), S_l^-(0)]\rangle \equiv \langle\langle S_i^+(t); S_l^-(0)\rangle\rangle\,, \tag{2.11}$$

$$G_{il}^-(t) = -i\theta(t)\langle[S_i^-(t), S_l^-(0)]\rangle \equiv \langle\langle S_i^-(t); S_l^-(0)\rangle\rangle\,, \tag{2.12}$$

where $\theta(t)$ is a unit step function and the canonical thermal average is indicated by the single angular brackets.

To calculate the Green's functions, we use the equation-of-motion method. The higher-order Green's functions are decoupled in the random phase approximation,

$$\langle\langle S_i^z(t)S_m^+(t); S_l^-(0)\rangle\rangle \xrightarrow[i\neq m]{} \langle S_i^z\rangle\langle\langle S_m^+(t); S_l^-(0)\rangle\rangle\,. \tag{2.13}$$

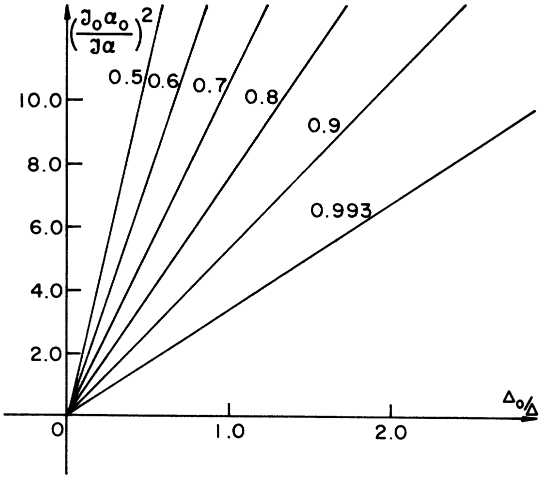

FIG. 1. Plot of $(\mathcal{J}_0\alpha_0/\mathcal{J}\alpha)^2$ vs Δ_0/Δ of the critical condition for the onset of local self-polarization predicted by the molecular-field approximation. A simple-cubic lattice is assumed. The curves are labeled by the host parameter A. Local self-polarization occurs in the region above the corresponding straight line.

Then the equations are solved in terms of the combined Green's functions,

$$\mathcal{G}^{+}_{il}(t) \equiv G^{+}_{il}(t) + G^{-}_{il}(t) \qquad (2.14a)$$

and

$$\mathcal{G}^{-}_{il}(t) \equiv G^{+}_{il}(t) - G^{-}_{il}(t)\ . \qquad (2.14b)$$

In the energy Fourier space, $\mathcal{G}^{+}_{il}(E)$ satisfies the equation

$$\frac{1}{\Delta}\left(\frac{E^2}{\Delta_i^2} - \Delta_i\right)\mathcal{G}^{+}_{il} + \frac{8\mathcal{J}\alpha^2}{\Delta}\ \langle S^z_i\rangle \sum_\delta \mathcal{G}^{+}_{i+\delta,l} - \frac{8\mathcal{J}\alpha^2}{\Delta}\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha} - 1\right)$$

$$\times \sum_\delta \left[\langle S^z_\delta\rangle \mathcal{G}^{+}_{0l}\Delta_{i,\delta} + \langle S^z_0\rangle \mathcal{G}^{+}_{\delta l}\Delta_{i,0}\right] = -\frac{\mathcal{E}_i}{\Delta}\ \langle S^z_i\rangle\, \Delta_{i,l}\ , \qquad (2.15)$$

where we have defined $\mathcal{E}_i = (1/\pi)(1 + E/\Delta_i)$; for a host ion, $\mathcal{E}_i = (1/\pi)(1 + E/\Delta)$, and for the impurity ion, $\mathcal{E}_0 = (1/\pi)(1 + E/\Delta_0)$.

$\mathcal{G}^{-}_{il}$ is related to $\mathcal{G}^{+}_{il}$,

$$\mathcal{G}^{-}_{il} = \frac{-1}{\pi\Delta_i}\ \langle S^z_i\rangle \Delta_{il} + \frac{E}{\Delta_i}\ \mathcal{G}^{+}_{il}\ . \qquad (2.16)$$

Before solving Eq. (2.15), we recall that for a pure crystal, that is, taking $\Delta_i = \Delta$, $\mathcal{J}_0\alpha_0 = \mathcal{J}\alpha$, and $\langle S^z_i\rangle = \langle S^z\rangle$, the Green's function was found[6] to be

$$\mathcal{G}^{0+}_{il} = \frac{\langle S^z\rangle(E+\Delta)}{\pi N}\sum_{\vec{k}} \frac{e^{i\vec{k}\cdot(\vec{i}-\vec{l})}}{E^2 - E^2_{\vec{k}}}\ , \qquad (2.17a)$$

where

$$E^2_{\vec{k}} = \Delta^2(1 - 2\langle S^z\rangle A\gamma_{\vec{k}}) \qquad (2.17b)$$

gives the dispersion relation of the collective excitation modes in the pure crystal. To solve for the perturbed Green's function $\mathcal{G}^{+}_{il}$ we first define

$$\epsilon_i = \langle S^z_i\rangle / \langle S^z\rangle - 1\ , \qquad (2.18)$$

where $\langle S^z\rangle$ is the value in the pure crystal (or the value for an ion at long distance from the impurity in an impure crystal). Equation (2.15) can be written

$$\left(\frac{E^2}{\Delta^2} - 1\right)\mathcal{G}^{+}_{il} + \frac{8\mathcal{J}\alpha^2\langle S^z\rangle}{\Delta}\sum_\delta \mathcal{G}^{+}_{i+\delta,l} = \frac{T_{il}}{\Delta}\ , \qquad (2.19)$$

where the impurity term T_{il} is

$$\frac{1}{\Delta}T_{il} = \langle S^z\rangle\Bigg[(1+\epsilon_i)\mathcal{E}_i\,\Delta_{il} + \frac{1}{\langle S^z\rangle}\left(\frac{\Delta_0}{\Delta} - 1\right)\Delta_{i,0}\mathcal{G}^{+}_{il}$$

$$- \frac{E^2}{\Delta^2}\left(\frac{\Delta}{\Delta_i} - 1\right)\mathcal{G}^{+}_{il} - \frac{8\mathcal{J}\alpha^2}{\Delta}\ \epsilon_i\sum_\delta \mathcal{G}^{+}_{i+\delta,l} - \frac{8\mathcal{J}\alpha^2}{\Delta}$$

$$\times\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha} - 1\right)\sum_\delta\left[\Delta_{i,\delta}\mathcal{G}^{+}_{0,l} + \Delta_{i,0}\mathcal{G}^{+}_{\delta l}(1+\epsilon_i)\right]\Bigg]\ . \qquad (2.20)$$

Noticing that the left-hand side of Eq. (2.19) is identical to the left-hand side of a corresponding equation for the pure-crystal Green's function $\mathcal{G}^{0+}_{il}$, we can express $\mathcal{G}^{+}_{il}$ in terms of $\mathcal{G}^{0+}_{il}$:

$$\mathcal{G}^{+}_{il} = \frac{\pi}{\langle S^z\rangle}\left(1 + \frac{E}{\Delta}\right)^{-1}\sum_j \mathcal{G}^{0+}_{ij}T_{jl}\ . \qquad (2.21)$$

If ϵ_i is limited in range, being appreciable only in the vicinity of the impurity, T_{jl} is essentially zero outside a small cluster of ions centered at the impurity and the summation in Eq. (2.21) is limited. This enables us to solve for the $\mathcal{G}^{+}_{il}$ easily as they are related to each other by a finite number of linear equations. The approximation that $\langle S^z_i\rangle$ deviates from $\langle S^z\rangle$ (the value for the pure host) only in the vicinity of the impurity has been fully discussed by Hone, Callen, and Walker[2] for a fixed spin system. We believe that a similar argument applies to the present system, and we shall adopt the approximation that $\epsilon_i = 0$ for all the host ions. We then only have to solve a set of $z+1$ equations. Finally, $\langle S^z_0\rangle = \langle S^z\rangle(1+\epsilon_0)$ is determined self-consistently from $\mathcal{G}^{+}_{00}$. We postpone its discussion to the end of this section.

The $z+1$ equations maybe written in matrix form

$$M\mathcal{G}^{+} = X\ , \qquad (2.22)$$

with the solution for $\mathcal{G}^{+}$ as

$$\mathcal{G}^{+} = M^{-1}X\ . \qquad (2.23)$$

Here $\mathcal{G}^{+}$ is a 1 by $z+1$ matrix, M is $z+1$ by $z+1$, and X is $z+1$ by 1. The explicit form of M can be obtained from Eqs. (2.21) and (2.20). Equation (2.23) can also be written

$$\mathcal{G}^{+}_{il} = \sum_j \frac{(-1)^{i+j}\mathrm{Minor}(M_{ji})}{\det|M|}\, X_{jl}\ , \qquad (2.24)$$

where the summation is over the $z+1$ sites centered at the impurity. The impurity modes are at the poles of $\mathcal{G}^{+}_{il}$ that are not common to $\mathcal{G}^{0+}_{il}$, i.e., they are given by the zeros of $\det|M|$. To find these zeros we first utilize the symmetry of the impurity cluster to block diagonalize M. This can be accomplished by a unitary transformation

$$M' = \nu^{-1}M\nu\ . \qquad (2.25)$$

Since $\det|M'| = \det|M|$, the zeros of $\det|M|$ are correctly given by the zeros of the determinant of the block-diagonalized matrix M'. Furthermore, the unitary matrix ν reveals the symmetry properties of the various impurity modes. To exhibit the explicit results, the crystal structure must be specified. We choose the simple-cubic lattice for this calculation. The unitary matrix ν is then[1]

$$\nu=(12)^{-1/2}\begin{bmatrix} 12^{1/2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 2^{1/2} & 6^{1/2} & 0 & 0 & 0 & 2 \\ 0 & 2^{1/2} & -6^{1/2} & 0 & 0 & 0 & 2 \\ 0 & 2^{1/2} & 0 & 6^{1/2} & 0 & 3^{1/2} & -1 \\ 0 & 2^{1/2} & 0 & -6^{1/2} & 0 & 3^{1/2} & -1 \\ 0 & 2^{1/2} & 0 & 0 & 6^{1/2} & -3^{1/2} & -1 \\ 0 & 2^{1/2} & 0 & 0 & -6^{1/2} & -3^{1/2} & -1 \end{bmatrix}, \tag{2.26}$$

which consists of two basis vectors of *s* symmetry, three of *p* symmetry, and two of *d* symmetry. The matrix equation (2.22) in the new coordinates is then

$$\mathcal{G}^{+\prime}=(M')^{-1}X' \ , \tag{2.27}$$

where

$$\mathcal{G}^{+\prime}=\nu^{-1}\mathcal{G}^{+} \tag{2.28a}$$

and

$$X'=\nu^{-1}X \ . \tag{2.28b}$$

The explicit expressions of M' and X' are

$$M'_{00}=-\mathcal{E}'_0\mathcal{E}^{-1}\mathcal{G}^{0+}_{00}+48\mathcal{J}_0\alpha_0\alpha\mathcal{E}^{-1}\mathcal{G}^{0+}_{06}+1 \ , \tag{2.29a}$$

$$M'_{01}=8(6)^{1/2}\,\alpha j_0\mathcal{E}^{-1}\mathcal{G}^{0+}_{00} \ , \tag{2.29b}$$

$$M'_{10}=6^{1/2}\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\,\mathcal{E}'-\mathcal{E}'_0\right)\mathcal{G}^{0+}_{06} \ , \tag{2.29c}$$

$$M'_{11}=1+48\alpha j_0\mathcal{E}^{-1}\mathcal{G}^{0+}_{06} \ , \tag{2.29d}$$

$$M'_{ii}=1 \quad (i\neq 1) \ , \tag{2.29e}$$

$$M'_{ii'}=0 \quad (i\neq i',\ i,\ i'\neq 1) \ , \tag{2.29f}$$

and

$$(X')^{l}_{i}=\sum_j(\nu^{-1})_{ij}\,\frac{1+E/\Delta_l}{1+E/\Delta}\,(1+\epsilon_0\Delta_{0,l})\mathcal{G}^{0+}_{jl} \ , \tag{2.30}$$

where

$$\mathcal{E}'_0=\frac{\Delta_0^2-E^2}{\Delta_0\langle S^z\rangle} \ , \quad \mathcal{E}'=\frac{\Delta^2-E^2}{\Delta\langle S^z\rangle} \ ,$$

and

$$j_0=\mathcal{J}_0\alpha_0(1+\epsilon_0)-\mathcal{J}\alpha \ .$$

It can be shown easily that

$$\mathcal{G}^{0+}_{06}=\frac{1}{48\mathcal{J}\alpha^2}\,(\mathcal{E}'\mathcal{G}^{0+}_{00}+\mathcal{E}) \ . \tag{2.31}$$

Therefore we need only calculate a single host Green's function $\mathcal{G}^{0+}_{00}$ numerically to find all the matrix elements of M'. This is true only in the present approximation of zero range in ϵ_i. The impurity-mode energies and symmetries can now be obtained from $\det|M|$ and the matrix ν and will be discussed in Sec. III.

We turn now to a discussion of the calculation of $\langle S^z\rangle$. For spin $\frac{1}{2}$, $S^z=\frac{1}{2}-S^-S^+$, so we seek

$$\langle S^z_i\rangle=\tfrac{1}{2}-\langle S^-_iS^+_i\rangle \ . \tag{2.32}$$

The correlation function $\langle S^-S^+\rangle$ can be expressed in terms of G^+ which is related to $\mathcal{G}^{\pm}$ by Eq. (2.14); finally $\mathcal{G}^-$ is related to $\mathcal{G}^+$ by Eq. (2.16). We obtain, at temperature T,

$$\langle S^z_0\rangle=\tfrac{1}{2}+\pi\int_{-\infty}^{\infty}\frac{\mathrm{Im}(\mathcal{G}^{+}_{00})\mathcal{E}_0}{e^{E/k_BT}-1}\,dE \ . \tag{2.33}$$

The explicit expression for $\mathcal{G}^{+}_{00}$ will be given and discussed in Sec. III, as its structure depends on the energies of the impurity modes. It is interesting to note that the contribution of the integration for negative energy in Eq. (2.33) gives the zero-temperature pseudospin deviation similar to the phenomena in an ordinary antiferromagnet or that of a pure induced moment system discussed in Ref. 6. The integrand of Eq. (2.33) involves $\langle S^z_0\rangle$, hence this quantity must be determined self-consistently. A numerical calculation of $\langle S^z_0\rangle$ for various temperatures and values of the impurity parameters is given in Sec. IV.

III. IMPURITY MODES AND LOCAL SUSCEPTIBILITIES

Similar to the ordinary ordered magnetic systems containing impurities,[1-3] an impure induced moment system exhibits local modes outside the excitation wave band or resonance modes in the band. The local-mode energies are given by the zeros of $\det|M'|$, as shown in Sec. II, and M' is pure real in this case. On the other hand, at a resonance-mode energy, the pure-crystal Green's functions, and hence M', have both real and imaginary parts. The energy of the resonance mode is given approximately by $\mathrm{Re}\det|M'|=0$, with the imaginary part defining a width or lifetime of the excitation due to the presence of nearby host states into which it may decay. (A more detailed description of the appearance of resonance modes has been given by Wolfram and Callaway.[1]) Thus, for both cases we find the energies of the impurity modes by taking

$$\mathrm{Re}\det|M'|=D_sD_p^3D_d^2=0 \ , \tag{3.1}$$

where $D_p=M'_{ii}$ $(i=2,\ 3,\ 4)$, $D_d=M'_{ii}$ $(i=5,\ 6)$, and

$$D_s=\det\begin{vmatrix} M'_{00} & M'_{01} \\ M'_{10} & M'_{11}\end{vmatrix} \ . \tag{3.2}$$

The components of M' are given by Eq. (2.29). We see that $D_p=D_d=1$, so that there are neither *p*- nor *d*-type impurity modes in our model. There may be *s*-type resonance or local modes, depending, respectively, on whether the zeros of $\mathrm{Re}D_s$ fall inside or outside the host-excitation-wave energy band; two *s*-type modes are predicted. It should be noted that, in fact, the above discussion can be shown to be true for a general lattice.

The energies of impurity modes of s-symmetry are given by the vanishing of $\mathrm{Re}D_s$. It can be written in the following form, revealing clearly the dependence of the energies on the impurity parameters $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ and Δ_0/Δ:

$$\left[\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\right)^2 \frac{\langle S_0^z\rangle}{\langle S^z\rangle}\left(1-\frac{E^2}{\Delta^2}\right)-\frac{\Delta}{\Delta_0}\left(\frac{\Delta_0^2}{\Delta^2}-\frac{E^2}{\Delta^2}\right)\right]$$

$$\times\frac{\Delta\pi}{1+E/\Delta}\ \frac{\mathcal{G}_{00}^{0+}}{\langle S^2\rangle}+\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\right)^2\frac{\langle S_0^z\rangle}{\langle S^z\rangle}=0\ . \qquad (3.3)$$

The fact that the exchange-interaction parameters $\mathcal{J}$ and $\mathcal{J}_0$ enter the equation as squared quantities shows that the exchange couplings can be either ferromagnetic or antiferromagnetic and the s-type impurity modes will appear at the same energies. (The relative phases of the pseudospins of the impurity and its set of nearest neighbors will be interchanged as the sign of the ratio $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ is reversed, as discussed in Sec. IV.) We note that by setting $E=0$ in Eq. (3.3), we easily recover the self-polarization criterion, Eq. (2.9), with the self-consistently calculated ratio $\langle S^z\rangle/\langle S_0^z\rangle$ replacing the corresponding molecular-field approximation result. The ratio $\langle S^z\rangle/\langle S_0^z\rangle$ is not unity in general even at $T=0$ because of the different zero-point fluctuations on the host and the impurity ions; this is in contrast to the molecular-field theory as shown in Eq. (2.8).

We see that $\langle S^z\rangle$ and $\langle S_0^z\rangle$ are required in order to determine the energies of the impurity modes. $\langle S^z\rangle$ depends only on the pure-host crystal and its calculation has been given by Wang and Cooper.[6] $\langle S_0^z\rangle$ is obtained from expression (2.33), where $\mathrm{Im}(\mathcal{E}_0\mathcal{G}_{00}^{+})$ has the form

$$\mathrm{Im}(\mathcal{E}_0\mathcal{G}_{00}^{+})$$

$$=\frac{\mathcal{E}_0^2\langle S_0^z\rangle}{\langle S^z\rangle}\ \frac{[-\mathrm{Re}(\mathcal{E}^{-1}\mathcal{G}_{00}^{0+})\,\mathrm{Im}D_s+\mathrm{Im}(\mathcal{E}^{-1}\mathcal{G}_{00}^{0+})\mathrm{Re}D_s]}{(\mathrm{Re}D_s)^2+(\mathrm{Im}D_s)^2} \qquad (3.4)$$

for E in the host excitation wave band and

$$\mathrm{Im}(\mathcal{E}_0\mathcal{G}_{00}^{+})=-\pi\mathcal{E}_0^2\frac{\langle S_0^z\rangle}{\langle S^z\rangle}\mathrm{Re}(\mathcal{E}^{-1}\mathcal{G}_{00}^{0+})$$

$$\times\sum_s\left(\delta(E-E_s)\Big/\left|\frac{d}{dE}(\mathrm{Re}D_s)\right|\right)\mathrm{sgn}(\eta\mathcal{E}'-\mathcal{E}_0')\ , \qquad (3.5)$$

where

$$\eta=\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\right)^2\langle S_0^z\rangle/\langle S^z\rangle \qquad (3.6)$$

for E outside the host energy band, where the summation is over the s-type local modes. The real and imaginary parts of D_s are

$$\mathrm{Re}D_s=(\eta\mathcal{E}'-\mathcal{E}_0')\,\mathrm{Re}(\mathcal{E}^{-1}\mathcal{G}_{00}^{0+})+\eta\ , \qquad (3.7a)$$

$$\mathrm{Im}D_s=(\eta\mathcal{E}'-\mathcal{E}_0')\,\mathrm{Im}(\mathcal{E}^{-1}\mathcal{G}_{00}^{0+})\ . \qquad (3.7b)$$

As it is clear that the local-mode energies depend on $\langle S_0^z\rangle$, which in turn depends on the local-mode energies, a self-consistent procedure is necessary to determine both quantities simultaneously. The numerical work and a quantitative discussion are presented in Sec. IV.

The quantity $\langle S_0^z\rangle$, which measures the population of excitations at the impurity site, is related to the local susceptibility at that site. This is of interest as the local susceptibility can be measured by NMR or Mössbauer techniques. In the present approximation it can be shown that the susceptibility of the impurity ion is

$$\chi_0=2\langle S_0^z\rangle(A_0\chi g_0/g+2g_0^2\mu_B^2\alpha_0^2/\Delta_0)\ , \qquad (3.8)$$

where χ is the susceptibility of a host ion,

$$\chi=\frac{2g^2\mu_B^2\alpha^2}{\Delta}\ \frac{2\langle S^z\rangle}{1-2\langle S^z\rangle}\ , \qquad (3.9)$$

and g and g_0 are the Landé g factors for the host and impurity ions, respectively. Measuring the susceptibilities in units of $2g^2\mu_B^2\alpha^2/\Delta$, we rewrite Eq. (3.8) as

$$\chi_0\Big/\left(\frac{2g^2\mu_B^2\alpha}{\Delta}\right)=2\langle S_0^z\rangle\left(\frac{\alpha_0}{\alpha}\right)\left(\frac{g_0}{g}\right)\left(\frac{\mathcal{J}_0\alpha_0}{\mathcal{J}\alpha}\right)$$

$$\times\left[\frac{2A\langle S^z\rangle}{1-2\langle S^z\rangle A}+\left(\frac{g_0}{g}\right)\right]. \qquad (3.10)$$

This expression shows that χ_0 depends on, in addition to the impurity parameters characterizing the impurity modes, two more impurity parameters α_0/α and g_0/g.

IV. NUMERICAL RESULTS AND DISCUSSIONS

The Green's functions describing the behavior of a two-level induced moment system containing a single two-level impurity have been calculated in Secs. II and III. In this section we select explicit examples to demonstrate the various impurity effects. Possible experiments are also discussed.

We choose for the host crystal a two-level induced moment system with $A\equiv4\mathcal{J}z\alpha^2/\Delta=0.993$. This is a close approximation to praseodymium, as this crystal may be a suitable paramagnetic host. The dispersion of the excitation wave energies has been found to be large and no magnetic ordering has been detected by neutron diffraction experiments on a single crystal Pr.[9] In reality, praseodymium has a more complicated structure; residing in a double-hexagonal close-packed lattice, half of the Pr ions have local environment of cubic symmetry and half have hexagonal symmetry. The two-level model in the present theory applies only

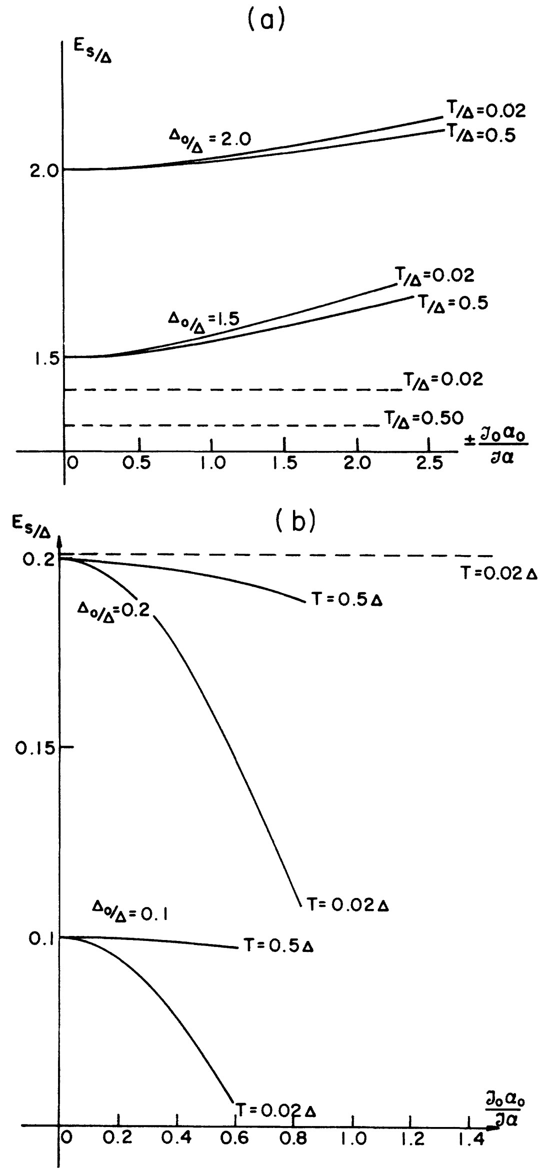

FIG. 2. Local-mode energy as function of $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$. The curves are labeled by the parameter Δ_0/Δ and temperature T/Δ. The host parameter $A = 0.993$. The dashed lines, labeled by temperature T/Δ, indicate the edge of the energy band of the host. (a) Local modes above the energy band. (b) Local modes in the gap.

to the ions of hexagonal sites. As we are not attempting a detailed study of any particular crystal, we will remain with the simplified model to avoid the formidable algebra.

The calculations of impurity-mode energies and of $\langle S_0^z \rangle$ for a specified host crystal require the two impurity parameters $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ and Δ_0/Δ. As discussed in Sec. III, local-mode energies and $\langle S_0^z \rangle$ are mutually dependent on each other and need to be determined simultaneously. We first calculate $\langle S^z \rangle$, which depends on the pure-crystal parameter A and the temperature measured in units of Δ, the crystal field splitting. $\mathrm{Re}\,\mathcal{G}_{00}^{0+}$ for energies outside the host energy band and $\mathrm{Re}\,\mathcal{G}_{00}^{0+}$ and $\mathrm{Im}\,\mathcal{G}_{00}^{0+}$ for energies in the band are then calculated. Energy derivatives of $\mathrm{Re}\,\mathcal{G}_{00}^{0+}$ are calculated for energies outside the band for use in computing the contribution to the integration of Eq. (2.33) due to the local modes. The integration is done using Simpson's rule. A value of $\langle S_0^z \rangle$ is chosen to start the process, and a new value of $\langle S_0^z \rangle$ is obtained after the process. Using the new value as the intial one, the process is repeated until a chosen convergence criterion is satisfied. The local-mode energies are obtained at the same time. Figures 2(a) and 2(b) show the local-mode energies as a function of ratio of impurity-host to host-host exchange interactions for various values of Δ_0/Δ and temperature. Figure 2(a) shows local modes above the energy band. This occurs when Δ_0 is close to or greater than the top of the host energy band. We recall that a limit has been imposed on the ratio $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ so that local self-polarization does not occur. This prevents the impurity mode from lying above the energy band for small values of Δ_0. However, it is seen that as temperature increases the top of the band as well as the local-mode energy is lowered, but the latter is less affected. It is therefore possible for an impurity mode to split off the energy band as temperature is increased, a phenomenon similar to that predicted for an ordinary impure spin system.[2] This is also true when the energy of the impurity mode is close to the bottom of the energy band; an impurity mode in the gap can split off from within the band as temperature is increased. The effects of a change of the impurity-host coupling on the energy of a local mode above the band is, however, opposite to that on the energy of a local mode in the gap shown in Fig. 2(a). As $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ increases the energy of a local mode above the band increases while the energy of a local mode in the gap decreases. This can be explained in a semiclassical picture of precessing pseudospins. (For an ordinary magnetic spin system, see Shiles and Hone.[15]) Evaluation of the matrix elements M'_{00}, M'_{01}, M'_{10}, and M'_{11} of Eqs. (2.29) shows that for ferromagnetic impurity-host exchange coupling the impurity pseudospin is 180° out of phase with its nearest-neighbor pseudospins for the above-band local modes and exactly in phase for the gap local modes. The opposite picture holds true for an antiferromagnetic impurity-host coupling. In either case an increase of the magnitude of $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$ drives the local-mode energies away from the host energy band as shown in Figs. 2(a) and 2(b). It is also to be noted that although only one localized mode occurs in each case shown in Figs. 2(a) and 2(b), it

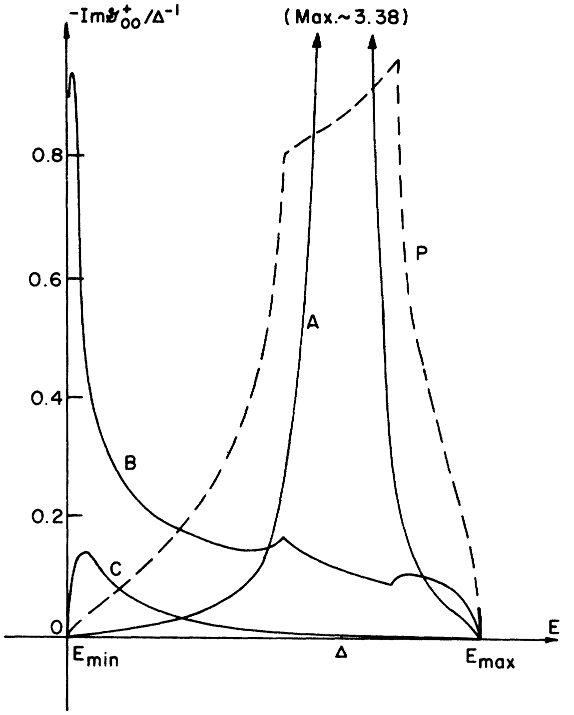

FIG. 3. Spectral weight function $\mathrm{Im}\mathcal{G}^{0+}_{00}/\Delta^{-1}$ inside the energy band ($T/\Delta = 0.02$, $A = 0.993$). Curve P corresponds to a pure crystal. Curve A shows the effect of reduction of impurity-host coupling. Curves B and C are cases when local mode occurs. There is a local mode above the band at 1.7Δ for B and a local mode in the gap at 0.11Δ for C.

is by no means true that the other impurity mode always resides in the energy band. It is possible for two local modes to appear in a system, one above the energy band and one in the gap. In this connection we examine the "spectral weight function" $\mathrm{Im}\mathcal{G}^{+}_{00}$ in Fig. 3. This quantity is not only indispensable in the calculation of $\langle S_0^z\rangle$ and the impurity-mode energies but also used along with the other Green's functions in determination of the cross section for neutron inelastic scattering on the impure system.[3] We have plotted only the positive-energy portion of the spectral weight function. The negative-energy portion which gives rise to zero-point excitation fluctuations is small and is only important at very low temperatures. The dashed curve corresponds to the pure crystal (i.e., $\Delta_0 = \Delta$, $\mathcal{J}_0\alpha_0 = \mathcal{J}\alpha$) at $T/\Delta = 0.02$. It shows the well-known Van Hove singularities. Assuming that the crystal field splitting of the impurity is the same as that of a host ion but the impurity-host coupling is reduced by a factor 2 from the host-host coupling, the spectral weight becomes narrowed, centered at $E = \Delta$ as shown in the same figure by the solid curve labeled A. As expected, it develops into a δ function as $\mathcal{J}_0\alpha_0$ approaches zero. Curve B corresponds to $\Delta_0 = 1.50$ and $\mathcal{J}_0\alpha_0 = 2.25\mathcal{J}\alpha$, a case where a local mode occurs above the energy band at $E = 1.7\Delta$. (The δ functions for local modes are not shown in the figure.) The large impurity-host coupling, which is near the limit imposed to restrain the system in a paramagnetic phase without local self-polarization, has shifted the local mode from 1.5Δ (when $\mathcal{J}_0\alpha_0 = 0$) to 1.7Δ, and at the same time pushed a large portion of the spectral weight inside the energy band to the bottom of the band. An increase of temperature and/or $J_0\alpha_0$ will enable an additional local mode to split off and appear in the gap as mentioned above. Curve C corresponds to a case with a local mode in the gap. The impurity crystal field splitting Δ_0 has been chosen to be just below the bottom of the band [$\Delta_0 = 0.2\Delta$, see Fig. 2(b)]. The large impurity-host coupling ($\mathcal{J}_0\alpha_0 = 0.8\mathcal{J}\alpha$) which shifts the local-mode energy to 0.11Δ has not been able to push the spectral weight too much from the bottom of the band.

Because of the fundamental role $\langle S_0^z\rangle$ plays in the impurity problems, we show, in Fig. 4, its temperature behavior for a few representative cases. The dashed curve representing $\langle S^z\rangle$ for a pure crystal is included for comparison. Solid curves A1 and A2 describe the cases when a local mode is above the band. We have taken $\Delta_0 = 1.5\Delta$ for both curves but $\mathcal{J}_0\alpha_0 = 0$ for A1 and $\mathcal{J}_0\alpha_0 = 2.25\mathcal{J}\alpha$ for A2. When $\mathcal{J}_0\alpha_0 = 0$ the zero-point excitation fluctuation vanishes and $\langle S_0^z\rangle = 0.5$ at $T = 0$. At finite temperature, it is given by

$$\langle S_0^z\rangle = \tfrac{1}{2}\tanh(\Delta_0/2k_BT)\,,$$

a result identical to that using the molecular-field approximation even in the presence of impurity-host coupling (i.e., $\mathcal{J}_0\alpha_0 \neq 0$), in the paramagnetic state. Thus, comparing A2 with A1 one sees the effects of the excitation waves calculated in the present Green's-function theory. As discussed previously in this section, the impurity-host coupling drives the local mode above the band to a higher energy and at the same time introduces spectral weight inside the band (for both positive and negative energy). The effects are: At low temperatures, appreciable zero-point excitation fluctuations reduce $\langle S_0^z\rangle$ from saturation; at high temperatures, the decrease of $\langle S_0^z\rangle$ is slowed down because of a higher-lying local mode. Curves B1 and B2 represent cases with a local mode in the energy gap. $\Delta_0 = 0.2\Delta$ for both curves, but $\mathcal{J}_0\alpha_0 = 0$ for B1 and $\mathcal{J}_0\alpha_0 = 0.8\mathcal{J}\alpha$ for B2. Similar arguments can be applied to understand the behavior. However, here B2 decreases more rapidly than B1 at $T \sim \Delta_0$ as the impurity-host coupling drives the local mode to a lower energy when the local mode is in the gap.

Local susceptibilities can be obtained from $\langle S_0^z\rangle$ and $\langle S^z\rangle$ according to Eqs. (3.8)–(3.10). Figure

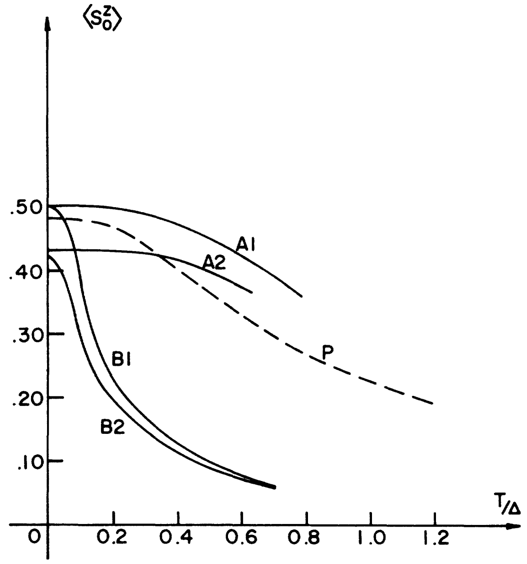

FIG. 4. $\langle S_0^z \rangle$ as a function of temperature. Curve P, the dashed line, for a pure system is also included for comparison. The effects of the impurity-host coupling are shown. The impurity parameters $(\Delta_0/\Delta, J_0\alpha_0/J\alpha)$ for A1 are (1.5, 0); A2, (1.5, 2.25); B1, (0, 2, 0); and B2, (0.2, 0.8). Comparing A1 with A2 or B1 with B2, one also sees the effects of collective waves, as A1 and B1 would be the results of neglecting the effects of collective excitations should there be finite impurity-host coupling (in the paramagnetic phase).

5 shows the temperature behavior of χ_0 in units of $2\mu_B^2 g^2\alpha/\Delta$, the susceptibility of a host ion at $T=0$ in the absence of exchange interaction. We have chosen $\mathcal{J}_0\alpha_0 = 0.5\mathcal{J}\alpha$, $\alpha_0=\alpha$, and $g_0 = g$ for our illustration, and the curves are labeled by Δ_0/Δ. The dashed curve represents the susceptibility of a host ion. $\Delta_0 = 0.2\Delta$ is a case where a local mode exists in the gap, while for $\Delta_0 = 1.5\Delta$ and $\Delta_0 = 2.0\Delta$ there are local modes above the energy band. $\Delta_0 = \Delta$ is a case with no localized modes. A comparison with the molecular-field theory is shown in Fig. 6 for $\Delta_0 = 0.2\Delta$ and $\Delta_0 = 1.5\Delta$. The susceptibilities calculated in the Green's-function theory are substantially lower. This is because in the molecular-field theory collective motions and short-range correlations are neglected. The error with the molecular-field theory is more serious the closer the exchange interaction of the host crystal ions is to the condition for magnetic ordering. In the same figure we also show the effects of the variation of impurity-host coupling by keeping Δ_0 constant. It is interesting to note that, from Eq. (3.10), for negative $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$, the local susceptibility at the impurity site χ_0 can be negative at low temperatures. This is possible when the first term in the parentheses is greater than the second term. It eventually becomes positive at high enough temperature.

In conclusion we remark on the experimental situation. There has been considerable increase of interest in induced moment systems recently. Praseodymium still appears to attract most of the attention. Specific-heat and susceptibility measurements[16,17] have been done on the powdered samples of Pr. Based on these, Bleaney[18] determined the crystal field energy-level schemes. He concluded that all Pr ions have a singlet crystal field ground state and that while a singlet first-excited state is predicted for ions on the hexagonal sites, the first-excited state for ions on cubic sites is a degenerate triplet. This, however, does not prevent the use of the present theory on the system in the paramagnetic phase, since the energy gap of the singlet and the triplet of the cubic ions is much larger than that between the two singlets of the hexagonal ions; the collective wave effects on the properties of a cubic ion will not be appreciable because of the existence of a large energy gap in the excitation wave spectrum. On the other hand, because of the fact that the exchange interaction between Pr ions is close to the ordering criterion, the collective wave will greatly affect the properties of the

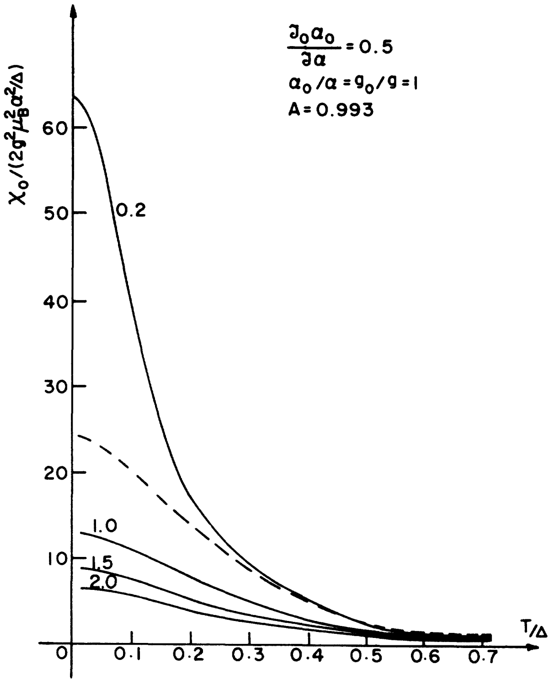

FIG. 5. Local susceptibilities at the impurity-ion site as function of temperature. This is directly proportional to the temperature-dependent part of the Knight shift observed in NMR. Here we show the effects of changing Δ_0/Δ with constant ratio $\mathcal{J}_0\alpha_0/\mathcal{J}\alpha$. The curves are labeled by the value of Δ_0/Δ. The dashed curve shows the temperature behavior of the local susceptibility of a host ion.

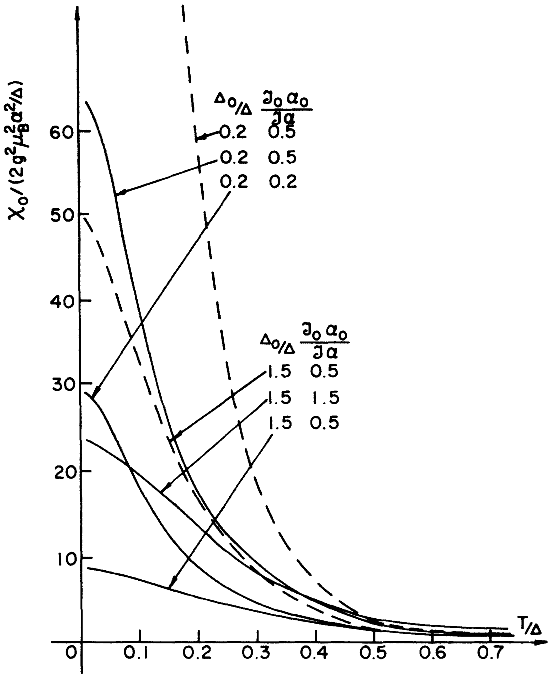

FIG. 6. Local susceptibilities at the impurity site as calculated by Green's-function theory (solid curves) are compared with those calculated using the molecular-field approximation (dashed curve). The effects of varying impurity-host coupling are also shown.

hexagonal ions. Indeed, neutron diffraction experiments[19] performed on polycrystalline Pr showed a rather complex antiferromagnetic structure with comparatively small ordered moments. Our theory developed in this paper therefore can only be applied to the polycrystalline Pr above its ordering temperature (~25 °K). On the other hand, neutron diffraction on a single-crystal[20] Pr shows that it is paramagnetic, and furthermore, neutron inelastic scattering[9] shows a large dispersion in the energies of the collective excitations on hexagonal sites and a large energy gap for the waves on the cubic sites. Hence single-crystal Pr provides an ideal example for the present theory. The impurity can be chosen from other rare-earth ions with integral J, as it was observed that the crystal field ground state of their compounds of NaCl structure with Group-V elements is generally a singlet.[21] In a more detailed calculation for Pr of double-hexagonal closed-packed structure, while Green's-function theory of this paper should be applied to the ions on hexagonal sites, a molecular-field approximation is sufficient for ions of cubic sites. To alter the situation a little, it is to be noted that very recent susceptibility[22] and magnetization measurements[23] on single-crystal Pr show a large anisotropy opposite to that predicted by Bleaney's theory with an isotropic exchange interaction. It has been suggested by Rainford[24] that the crystal field energy scheme of Bleaney is not correct. While the ground state of the ions remains as a singlet, the first-excited state of the ions on hexagonal sites may be a doublet instead of a singlet. There are many more rare-earth compounds, as the rare-earth Group-V compounds mentioned above, which can be used as host crystals for experimental study. The crystal field energy scheme is, however, in general, singlet-triplet instead of the simple singlet-singlet configuration. While the simple calculation is not applicable to account for the quantitative behavior, many of the qualitative features predicted here should remain.

As mentioned in Sec. I, it appears that neutron inelastic scattering is the most valuable technique in studying an impure induced moment system. Temperature variations of the local-mode energies along with temperature and impurity effects on the excitation wave energy band can be studied and compared with the theory.

NMR can be performed at the singlet ground-state ions in the paramagnetic state because the complete quenching of the ionic moment destroys the effective hyperfine field felt by the nucleus as discussed by Jones.[25] Indeed, Pr^{141} and Tm^{169} NMR in the paramagnetic compounds PrP, PrAs, TmP, TmAs, and TmSb have been observed and giant Knight shifts reported.[25] Since the temperature-dependent part of the Knight shift is proportional to the local susceptibility of the ion, this technique can also be useful in studying such impure induced moment systems as Tm-Pr-P mixed crystals, etc. Observing NMR in the anions may provide indirect information about the local susceptibilities at the impurity- and host-ion sites. Such experiments for ordinary magnetic systems with impurities have proved fruitful.[26] Mössbauer techniques, on a similar basis, may also be employed to measure the local susceptibilities and their temperature variations. The bulk susceptibility of an impure system could reveal some of the collective wave effects if the temperature and impurity-concentration dependence of such a quantity are analyzed. Bulk susceptibilities of the Pr-La system with variable La concentration have been measured.[27] A theoretical consideration of this particular induced moment system with vacancies will be given in a separate publication.

Finally, we mention that specific-heat measurement can also be a possibility in obtaining information from the impure system, especially when there is a local mode in the energy gap. A low-temperature anomaly characterizing the local mode could then be observed.

Note added in manuscript. P. Fulde and I. Peschel [Z. Physik 241, 82 (1971)] have discussed some of the topics of this work using a related method.

APPENDIX: NUMERICAL CALCULATION OF $\mathcal{G}_{00}^{0+}$

Equation (2.17) gives the expression for $\mathcal{G}_{ii}^{0+}$. We require numerical values only for $\mathcal{G}_{00}^{0+}$, which may be written

$$\mathcal{G}_{00}^{0+}=\frac{\langle S^z\rangle}{\pi N(E-\Delta)}\sum_{\vec{\kappa}}\frac{1}{1+\Omega_{\vec{\kappa}}(E)}\,, \qquad \text{(A1)}$$

where $\Omega_{\vec{\kappa}}(E)=2A\langle S^z\rangle\Delta^2\gamma_{\vec{\kappa}}/(E^2-\Delta^2)$. This expression has no poles for energy E outside the pure-crystal excitation energy band, so that at these energies the part under the $\vec{\kappa}$ summation may be expanded in a simple series in powers of $\Omega_{\vec{\kappa}}(E)$ [$|\Omega_{\vec{\kappa}}(E)|$ is always smaller than unity for energies outside the band]. We obtain

$$\mathcal{G}_{00}^{0+}=\frac{\langle S^z\rangle}{\pi(E-\Delta)}\sum_n C_n\Omega^{2n}\,, \qquad \text{(A2)}$$

where the odd-order terms are all zero, the C_n are constants, and $\Omega=2A\langle S^z\rangle\Delta^2/(E^2-\Delta^2)$. In the calculation of the results given below, we have taken the sum to $n=20$. We also calculated the energy derivative of $\mathcal{G}_{00}^{0+}$ outside the band, using a similar series. When the energy E is inside the band, the simple series is no longer valid. For these energies we first convert the summation in (A2) into an integration and perform the integration numerically using Gaussian quadratures.[28] Employing the method of Ref. 1, we express (A2) in terms of the Bessel function $J_0(\tau)$, reducing the triple integral (over the three components of $\vec{\kappa}$) to a single integral over τ. As mentioned earlier, $\mathcal{G}_{ii}^{0+}$ has both real and imaginary parts for energies in the host band (where $\mathcal{G}_{ii}^{0+}$ has poles):

$$\operatorname{Re}\mathcal{G}_{00}^{0+}=\frac{\langle S^z\rangle(E+\Delta)}{\pi C}\int_0^\infty d\tau\,\sin(\tilde{E}\tau)[J_0(\tau)]^3\,, \qquad \text{(A3)}$$

$$\operatorname{Im}\mathcal{G}_{00}^{0+}=\frac{\langle S^z\rangle(E+\Delta)}{\pi C}\int_0^\infty d\tau\,\cos(\tilde{E}\tau)[J_0(\tau)]^3\,, \qquad \text{(A4)}$$

where $C=16\mathcal{J}\alpha^2\Delta\langle S^z\rangle$ and $\tilde{E}=(E^2-\Delta^2)/C$. In the numerical integration we employ 1600 six-point quadratures, truncating the integral at $\tau=50$, and for $J_0(\tau)$ we use polynomial expressions[29] accurate to 10^{-8}. For a partial check on the results, we have also performed the numerical integration for some energies above the band and compared these results with those from the series calculation; the agreement was within 0.01% for energies not too close to the band (close to the band the series truncation may contribute a large error). Another check on the method is to calculate $\operatorname{Im}\mathcal{G}_{00}^{0+}$ above the band using expression (A4). These values were found to be very small compared to $\operatorname{Re}\mathcal{G}_{00}^{0+}$, as required (in an exact treatment $\operatorname{Im}\mathcal{G}_{00}^{0+}=0$ outside the band).

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