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Impurity Excitations in Induced-Moment Systems in the Paramagnetic Phase; Some Effects of Additional Exchange Coupling*

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The impurity excitations characteristic of a single impurity in a paramagnetic induced-moment crystal are examined in a model that includes second-neighbor exchange coupling. All ions are assumed to have a singlet crystal-field ground state and singlet lowest excited state. Earlier calculations assuming only nearest-neighbor exchange found only s-type impurity modes in this type of system. It is found that the more complex exchange coupling may introduce additional s-type modes, and under certain conditions modes of other symmetry may appear. The qualitative results are valid for a general lattice.

I. INTRODUCTION

Recently, Wang and Cooper[1] discussed, using Green's-function theory and a pseudospin formalism, the collective excitations that may be characteristic of pure induced-moment crystals. For the crystals in the paramagnetic phase, these excitations are magnetic excitons. More recently, several papers[2,3] examined the changes in the magnetic exciton spectrum when substitutional impurities are placed in a paramagnetic induced-moment system. The problem has also been discussed for the system in the ordered phase.[4] In Ref. 3, hereafter called I, it was found that only s-type impurity modes may appear in the paramagnetic system containing a single isolated impurity, under the assumption that only nearest-neighbor exchange coupling was important. This remained true regardless of lattice symmetry, as long as the only exchange coupling that changed upon substitution of the impurity was the coupling between the impurity and its nearest neighbors.

The present paper extends some of the work of I to second-neighbor exchange coupling. It is found that impurity modes of symmetry other than s (p, d, etc.) may appear; this occurs when more complex exchange coupling near the impurity is considered and/or the deviation of the expectation value of the z component of pseudospin, from the host value, is important on lattice sites other than the impurity site itself (this expectation value is a measure of the population of elementary excitations at a given site at a given temperature). We note that in I only the deviation at the impurity itself was included. A significant difference between the s-type modes and those of other symmetries, when examining the single isolated impurity problem, is that the s-type are the only modes in which the impurity itself participates. In the other modes, owing to symmetry considerations, only various neighboring ions have nonzero amplitude. This difference can manifest itself, for example, in inelastic neutron scattering, where modes that involve the isolated impurity have both coherent and incoherent contributions to the scattering cross section, while those that do not involve the impurity have only a coherent part[5,6] (the coherence is a result of scattering from two or more equivalent spins). We comment here that the farther neighbor effects can be important in induced moment crystals, since the rare-earth ions that form the magnetic lattice characteristically have long-range exchange coupling.

As in I, we employ the thermal Green's-function method in the random-phase approximation (RPA), using the pseudospin formalism,[1] and consider only two-state systems for both the impurity and the host ions. Only the single isolated impurity problem is studied; as shown in Ref. 5 for fixed-moment systems and discussed in Ref. 7 for a paramagnetic induced-moment system containing vacancy impurities, the single-impurity solution forms the basis of a solution, linear in the impurity concentration, for small impurity concentrations. We assume that the crystal is in the paramagnetic phase, which may include not only those systems that remain paramagnetic down to zero temperature, but also those systems, above their critical temperatures, that order at low enough temperatures. Exchange coupling to second-nearest neighbors is included in the calculation, and for simplicity we assume that all pure crystal exchange is ferromagnetic. The effect of even further-neighbor coupling is discussed briefly. Also we assume that the expectation value of the z component of pseudospin $\langle S_i^z \rangle$ differs from the pure host value $\langle S^z \rangle$ only on the impurity site $i=0$ and on the nearest-neighbor sites $i=\delta$. Extension of the detailed calculations to exchange coupling between ions further apart than second neighbors and/or to deviation of $\langle S_i^z \rangle$ at sites further from the impurity than its nearest neighbors only greatly increases the algebraic complexity but does not significantly add to the discussion of this paper. A general lattice is considered in the initial calculations, and the linear chain is discussed in detail as an illustration.

As expected, additional impurity modes appear when further-neighbor exchange is included. We find that, in our model, modes of other than s symmetry may be present when $\langle S_\delta^z \rangle - \langle S^z \rangle$ is nonzero and/or when the strength of the exchange coupling between two host ions in the vicinity of the impurity differs from the pure crystal exchange strength for the same pair of ions. Impurity-ion–host-ion exchange itself produces only s-type modes, as in the case of only nearest-neighbor exchange. We do not expect $\langle S_\delta^z \rangle$ to be very much different from the host value $\langle S^z \rangle$, so that impurity excitations that depend only on the parameter $\langle S_\delta^z \rangle - \langle S^z \rangle$ will not be expected to be localized. In contrast, the deviated host-host exchange parameter may in principle be quite different from the unperturbed value and may produce local modes. Certain experiments, for example neutron scattering and Raman scattering, can detect the number, the energies, and the symmetries of the modes (this is true even in those cases where the quantitative results cannot be examined precisely due to the large number of parameters and/or lack of knowledge about the system). This information may then be used to learn something about the exchange mechanisms in both the pure and the impure systems. For example, if the exchange coupling is of the Ruderman–Kittel–Kasuya–Yosida (RKKY) type, as in the rare-earth metals, we would expect any local modes to be only of s type, since the presence of the impurity may significantly affect the coupling between two host ions only if the coupling mechanism involves a path via the impurity (superexchange). In contrast, if a type of superexchange is important, local modes of non-s-type may be expected in certain systems.

In Sec. II we present the Green's-function formalism for a general lattice, and solve the equations in detail for the simple case of a linear chain. The results are discussed in Sec. III.

II. GREEN'S-FUNCTION FORMALISM

The Hamiltonian for an induced-moment system with zero applied external field, where only nearest-neighbor exchange between sites separated by vectors $\vec{\delta}$ and second-nearest-neighbor exchange between sites separated by vectors θ are considered to be important, is

$$\mathcal{H}=\sum_l V_{cl}-\sum_{l,\delta}\mathcal{J}_{l,l+\delta}\,\vec{J}_l\cdot\vec{J}_{l+\delta}-\sum_{l,\theta}\mathcal{J}_{l,l+\theta}\,\vec{J}_l\cdot\vec{J}_{l+\theta}\,. \tag{2.1}$$

V_{cl} is the single-ion crystal-field potential at ion l, which gives a singlet ground state and a singlet excited state separated by energy gap Δ for a host ion and Δ_0 for an impurity ion. The $\mathcal{J}_{l,m}$ are the exchange coupling parameters for the various pairs l, m, which are positive for ferromagnetic exchange. We assume that in the pure crystal the nearest-neighbor exchange has the value $\mathcal{J}_1$ and the second-nearest-neighbor exchange the value $\mathcal{J}_2$. When we substitute an impurity at site $l=0$ the following additional parameters are needed:

$$\mathcal{J}_{0\delta}=\mathcal{J}_1', \quad \mathcal{J}_{0\theta}=\mathcal{J}_2', \quad \mathcal{J}_{\delta,\delta'}=\mathcal{J}_2'' \quad (\delta'=\delta+\theta). \tag{2.2}$$

$\mathcal{J}_2''$ couples two ions, second neighbors to each other, that are both nearest neighbors to the impurity; this additional perturbed coupling cannot be ignored in a calculation that considers second-neighbor coupling to be important. Equation (2.2) is sufficient for many crystal lattices. In certain other crystals, for example hexagonal, an additional perturbed coupling, that between two ions that are nearest neighbors to each other and also nearest neighbors to the impurity, must be included. This latter term will lead to qualitative conclusions similar to that form the $\mathcal{J}_2''$ coupling, so for simplicity we will not include it, and discuss in detail only crystals that fall in the first category. The Hamiltonian (2.1) becomes

$$\begin{aligned}\mathcal{H}=&\sum_l V_{cl}-\mathcal{J}_1\sum_{l,\delta}\vec{J}_l\cdot\vec{J}_{l+\delta}-\mathcal{J}_2\sum_{l,\theta}\vec{J}_l\cdot\vec{J}_{l+\theta}\\&-2(\mathcal{J}_1'-\mathcal{J}_1)\sum_\delta\vec{J}_0\cdot\vec{J}_\delta-2(\mathcal{J}_2'-\mathcal{J}_2)\sum_\theta\vec{J}_0\cdot\vec{J}_\theta\\&-(\mathcal{J}_2''-\mathcal{J}_2)\sum_{\substack{\delta,\delta'\\(\delta+\theta=\delta')}}\vec{J}_\delta\cdot\vec{J}_{\delta'}\,.\end{aligned} \tag{2.3}$$

We assume the system to be in the paramagnetic phase; it can be shown that the criterion for ordering in the pure crystal (vanishing of the $\vec{k}=0$ mode energy, assuming a second-order phase transition) is that

$$(4\alpha^2\langle S^z\rangle/\Delta)(z_1\mathcal{J}_1+z_2\mathcal{J}_2)\geq 1, \tag{2.4}$$

where $\alpha=\langle 0_c|J^z|1_c\rangle$ is the matrix element of J^z between the crystal-field ground and excited states on a host ion, and z_1 and z_2 are, respectively, the numbers of first and second neighbors to an ion. Equation (2.3) may be expressed in pseudospin operators,[1] where, for the two-state systems, we define $S_l^z=\frac{1}{2}$ or $S_l^z=-\frac{1}{2}$ for ion l in the crystal-field ground state or excited state, respectively. We obtain, analogous to the corresponding expression in I,

$$\begin{aligned}\mathcal{H}=&-\Delta\sum_l S_l^z-(\Delta_0-\Delta)S_0^z-4\mathcal{J}_1\alpha^2\sum_{l,\delta}S_l^xS_{l+\delta}^x\\&-4\mathcal{J}_2\alpha^2\sum_{l,\theta}S_l^xS_{l+\theta}^x-8\alpha(\mathcal{J}_1'\alpha_0-\mathcal{J}_1\alpha)\sum_\delta S_0^xS_\delta^x\\&-8\alpha(\mathcal{J}_2'\alpha_0-\mathcal{J}_2\alpha)\sum_\theta S_0^xS_\theta^x\\&-4\alpha^2(\mathcal{J}_2''-\mathcal{J}_2)\sum_{\substack{\delta,\delta'\\(\delta+\theta=\delta')}}S_\delta^xS_{\delta'}^x,\end{aligned} \tag{2.5}$$

where α_0 is the off-diagonal matrix element at the impurity site.

As in I, we require the Green's function[8]

$$\begin{aligned}\mathcal{G}_{il}^+(t)&=\langle\langle S_i^+(t)+S_i^-(t);\,S_l^-(0)\rangle\rangle\\&=-i\Theta(t)\,\langle[S_i^+(t)+S_i^-(t),\,S_l^-(0)]\rangle,\end{aligned} \tag{2.6}$$

where $\Theta(t)$ is the unit step function and the angular brackets denote the thermal average. Using standard procedures, we write the equation of motion for $\mathcal{G}_{il}^+(t)$, decouple in the RPA, Fourier-transform to energy space, and obtain a set of algebraic equations for $\mathcal{G}_{il}^+=\mathcal{G}_{il}^+(E)$:

$$\begin{aligned}&\mathcal{E}_i'\mathcal{G}_{il}^++8\mathcal{J}_1\alpha^2(1+\sigma_i)\sum_\delta\mathcal{G}_{i+\delta,l}^++8\mathcal{J}_2\alpha^2(1+\sigma_i)\sum_\theta\mathcal{G}_{i+\theta,l}^+\\&\quad+8\alpha(\mathcal{J}_1'\alpha_0-\mathcal{J}_1\alpha)\sum_\delta[(1+\sigma_\delta)\mathcal{G}_{0l}^+\Delta_{i\delta}\\&\quad+(1+\sigma_0)\mathcal{G}_{\delta l}^+\Delta_{i0}]+8\alpha(\mathcal{J}_2'\alpha_0-\mathcal{J}_2\alpha)\sum_\theta[(1+\sigma_\theta)\mathcal{G}_{0l}^+\Delta_{i\theta}\\&\quad+(1+\sigma_0)\mathcal{G}_{\theta l}^+\Delta_{i0}]+8\alpha^2(\mathcal{J}_2''-\mathcal{J}_2)\\&\quad\times\sum_{\substack{\delta,\delta'\\(\delta+\theta=\delta')}}(1+\sigma_\delta)\mathcal{G}_{\delta l}^+\Delta_{i\delta'}=\Delta_{il}(1+\sigma_l)\,\mathcal{E}_l\,.\end{aligned} \tag{2.7}$$

We have defined the parameters $\sigma_i=\langle S_i^z\rangle/\langle S^z\rangle-1$, $\mathcal{E}_l=(E+\Delta_l)/(\pi\Delta_l)$, $\mathcal{E}_l'=(E^2-\Delta_l^2)/(\Delta_l\langle S^z\rangle)$, and Δ_{il} is the Kronecker Δ. Since σ_i may, in general, be nonzero for i arbitrarily far from the impurity, Eq. (2.7) will lead to a set of N equations in the N unknowns $\mathcal{G}_{il}$ (for i on any of the N ions in the crystal). The problem is made soluble by taking $\sigma_i\neq 0$ only for i confined to a certain small region near the impurity. In I we assumed $\sigma_i=0$ for $i\neq 0$, i.e., restricted this quantity to the impurity site only; this should be a good approximation when only nearest-neighbor exchange coupling is considered. Reference 9, for example, calculates the quantity analogous to σ_δ for fixed spin systems with only nearest-neighbor exchange and shows it to be small. For appreciable further-neighbor coupling, one should expect σ_i to be important on some of the host sites near the impurity. In the present work we take $\sigma_i=0$ for $i\neq 0, \delta$ and therefore must determine self-consistently the quantities σ_0 and σ_δ (note that owing to symmetry all σ_δ are the same).

This should be a good approximation for our model, and in any case will be sufficient to illustrate the appearance of additional impurity modes. The set of equations becomes, after separating the impurity parts from the pure crystal parts, with $\mathcal{E}=(E+\Delta)/(\pi\Delta)$ and $\mathcal{E}'=(E^2-\Delta^2)/(\Delta\langle S^z\rangle)$,

$$\mathcal{E}'\mathcal{G}^+_{il}+8\mathcal{J}_1\alpha^2\sum_{\delta}\mathcal{G}^+_{i+\delta,l}+8\mathcal{J}_2\alpha^2\sum_{\theta}\mathcal{G}^+_{i+\theta,l}=\mathcal{E}\,\Delta_{il}+P_{il}, \qquad (2.8)$$

where the perturbation term P_{il} is

$$\begin{aligned}P_{il}={}&\Delta_{il}[(1+\sigma_l)\mathcal{E}_l-\mathcal{E}]+(\mathcal{E}'-\mathcal{E}'_i)\mathcal{G}^+_{il}-8\alpha^2\sigma_0\Delta_{i0}\Big(\mathcal{J}_1\sum_{\delta}\mathcal{G}^+_{i+\delta,l}+\mathcal{J}_2\sum_{\theta}\mathcal{G}^+_{i+\theta,l}\Big)\\&-8\mathcal{J}_1\alpha^2\sigma_\delta\Big(\sum_{\delta'}\Delta_{i\delta'}\Big)\sum_{\delta}\mathcal{G}^+_{i+\delta,l}-8\mathcal{J}_2\alpha^2\sigma_\delta\Big(\sum_{\delta'}\Delta_{i\delta'}\Big)\sum_{\theta}\mathcal{G}^+_{i+\theta,l}-8\alpha(\mathcal{J}'_1\alpha_0-\mathcal{J}_1\alpha)\\&\times\sum_{\delta}[(1+\sigma_\delta)\mathcal{G}^+_{0l}\Delta_{i\delta}+(1+\sigma_0)\mathcal{G}^+_{\delta l}\Delta_{i0}]-8\alpha(\mathcal{J}'_2\alpha_0-\mathcal{J}_2\alpha)\sum_{\theta}[\mathcal{G}^+_{0l}\Delta_{i\theta}+(1+\sigma_0)\mathcal{G}^+_{\theta l}\Delta_{i0}]\\&-8\alpha^2(\mathcal{J}''_2-\mathcal{J}_2)(1+\sigma_\delta)\sum_{\substack{\delta,\delta'\\(\delta+\theta=\delta')}}\mathcal{G}^+_{\delta,l}\Delta_{i\delta'}. \qquad (2.9)\end{aligned}$$

For $P_{il}=0$, the solutions to (2.8) are the pure crystal Green's functions $\mathcal{G}^{0+}_{il}$, which have the form

$$\mathcal{G}^{0+}_{il}=\frac{(E+\Delta)\langle S^z\rangle}{\pi N}\sum_{\vec{k}}\frac{e^{i\vec{k}\cdot(\vec{l}-\vec{i})}}{E^2-E^2_{\vec{k}}}, \qquad (2.10)$$

where the sum is over the first Brillouin zone, $E^2_{\vec{k}}=\Delta^2-8z_1\mathcal{J}_1\alpha^2\Delta\langle S^z\rangle\gamma^{(1)}_{\vec{k}}-8z_2\mathcal{J}_2\alpha^2\Delta\langle S^z\rangle\gamma^{(2)}_{\vec{k}}$ is the dispersion relation for the pure crystal, z_1 and z_2 are the number of first and second neighbors, respectively, $\gamma^{(1)}_{\vec{k}}=\sum_\delta e^{i\vec{k}\cdot\vec{\delta}}/z_1$, and $\gamma^{(2)}_{\vec{k}}=\sum_\theta e^{i\vec{k}\cdot\vec{\theta}}/z_2$.

We can now express $\mathcal{G}^+_{il}$ in terms of $\mathcal{G}^{0+}_{il}$:

$$\mathcal{G}^+_{il}=(1/\mathcal{E}\langle S^z\rangle)\sum_{j}\mathcal{G}^{0+}_{ij}(\mathcal{E}\,\Delta_{jl}+P_{jl}). \qquad (2.11)$$

Owing to the restrictions on the spatial extent of j in P_{jl} for our localized perturbation, (2.11) is, when i is restricted to the perturbed cluster of ions, a finite set of algebraic equations in the unknowns $\mathcal{G}^+_{il}$. We obtain, with $\epsilon_1=\mathcal{J}'_1\alpha_0-\mathcal{J}_1\alpha$, $\epsilon_2=\mathcal{J}'_2\alpha_0-\mathcal{J}_2\alpha$, and $\epsilon''_2=\mathcal{J}''_2\alpha-\mathcal{J}_2\alpha$,

$$\begin{aligned}\mathcal{E}\langle S^z\rangle\mathcal{G}^+_{il}={}&\mathcal{E}_l(1+\sigma_l)\mathcal{G}^{0+}_{il}+(\mathcal{E}'-\mathcal{E}'_0)\mathcal{G}^{0+}_{i0}\mathcal{G}^{0+}_{0l}-8\alpha^2\sigma_0\mathcal{G}^{0+}_{i0}\Big(\mathcal{J}_1\sum_{\delta}\mathcal{G}^+_{\delta l}+\mathcal{J}_2\sum_{\theta}\mathcal{G}^+_{\theta l}\Big)\\&-8\alpha\epsilon_1\Big[(1+\sigma_\delta)\Big(\sum_{\delta}\mathcal{G}^{0+}_{i\delta}\Big)\mathcal{G}^+_{0l}+(1+\sigma_0)\mathcal{G}^{0+}_{i0}\sum_{\delta}\mathcal{G}^+_{\delta l}\Big]-8\alpha\epsilon_2\Big[\Big(\sum_{\theta}\mathcal{G}^{0+}_{i\theta}\Big)\mathcal{G}^+_{0l}+(1+\sigma_0)\mathcal{G}^{0+}_{i0}\sum_{\theta}\mathcal{G}^+_{\theta l}\Big]\\&-8\mathcal{J}_1\alpha^2\sigma_\delta\sum_{\delta,\delta'}\mathcal{G}^{0+}_{i\delta'}\mathcal{G}^+_{\delta'+\delta,l}-8\mathcal{J}_2\alpha^2\sigma_\delta\sum_{\delta,\theta}\mathcal{G}^{0+}_{i\delta}\mathcal{G}^+_{\delta+\theta,l}-8\alpha\epsilon''_2(1+\sigma_\delta)\sum_{\substack{\delta,\delta'\\(\delta+\theta=\delta')}}\mathcal{G}^{0+}_{i\delta'}\mathcal{G}^+_{\delta l}. \qquad (2.12)\end{aligned}$$

We note here that the lattice has not yet been specified. If this expression is symmetric with respect to the nearest-neighbor indices δ and also with respect to the second-nearest-neighbor indices θ, only s-type impurity modes may characterize the system. In I the corresponding expression displays this symmetry, as can be seen by examining the expression T_{il} in that work for the case $\langle S^z_i\rangle-\langle S^z\rangle=0$ for $i\neq 0$. In the present work the required symmetry holds only if the last three terms in (2.12) are zero; in that case the inclusion of second-nearest-neighbor coupling introduces only additional s-type modes. Modes of other symmetry may appear only if $\sigma_\delta\neq 0$ and/or $\epsilon''_2\neq 0$.

A detailed analysis requires that the lattice be specified. As an illustration we examine the simple case of a linear chain. The perturbed cluster consists of seven ions, the impurity at site 0, the nearest neighbors at $\delta=1, 2$, the second neighbors at $\theta=3, 4$, and the third neighbors at sites $\tau=5, 6$. The ions at sites τ are included because these sites are coupled to the sites δ by the host exchange coupling $\mathcal{J}_2$, so that the former are directly affected by the perturbed population term σ_δ. The impurity exchange parameter $\mathcal{J}'_1$ couples the impurity with site 1 and with site 2, the parameter $\mathcal{J}'_2$ couples the impurity with site 3 and with site 4, and parameter $\mathcal{J}''_2$ couples site 1 with site 2. The set of equations (2.12) thus has dimensions 7×7; it can be written in matrix form

$$M\mathcal{G}^+=X, \qquad (2.13)$$

where

$$X_{il}=\mathcal{E}_l\mathcal{G}^{0+}_{il}(1+\sigma_l)/\mathcal{E}\langle S^z\rangle.$$

The solutions are

$$\mathcal{G}^+_{il} = \sum_j (-1)^{i+j} \frac{\text{minor}(M_{ij})}{\det|M|} X_{jl} . \tag{2.14}$$

The impurity modes are found at the poles of $\mathcal{G}^+_{ii}$ that are not common to the pure crystal, that is, at the energy zeroes of the real part of det$|M|$. To facilitate the separation into the various modes it is usual to transform from a basis of individual lattice sites to a new basis consisting of linear combinations of the sites, these linear combinations having the symmetries of the various impurity modes. We use group theory to find the unitary matrix v, where $M' = v^{-1}Mv$ is block diagonal. det$|M'|$ ($=$det$|M|$) is then easily factored, and equating the various factors individually to zero allows determination of the impurity mode energies. We find for v

$$v = 2^{-1/2} \begin{pmatrix} 2^{1/2} & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & -1 \end{pmatrix} . \tag{2.15}$$

v has four s-type basis vectors and three p-type vectors. M' is then

$$M' = \begin{pmatrix} M'_{00} & M'_{01} & M'_{02} & M'_{03} & 0 & 0 & 0 \\ M'_{10} & M'_{11} & M'_{12} & M'_{13} & 0 & 0 & 0 \\ M'_{20} & M'_{21} & M'_{22} & M'_{23} & 0 & 0 & 0 \\ M'_{30} & M'_{31} & M'_{32} & M'_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & M'_{44} & M'_{45} & M'_{46} \\ 0 & 0 & 0 & 0 & M'_{54} & M'_{55} & M'_{56} \\ 0 & 0 & 0 & 0 & M'_{64} & M'_{65} & M'_{66} \end{pmatrix} , \tag{2.16}$$

where

$$\begin{aligned}
M'_{00} &= 1 + \overline{\mathcal{E}}\,\mathcal{G}^{0+}_{00} + (\overline{\alpha}/\alpha)(z_1 \rho_1 \mathcal{G}^{0+}_{0\delta} + z_2 \epsilon_2 \mathcal{G}^{0+}_{0\theta}), \\
M'_{10} &= \sqrt{2}\,\{\overline{\mathcal{E}}\,\mathcal{G}^{0+}_{0\delta} + (\overline{\alpha}/\alpha)[\epsilon_2 \mathcal{G}^{0+}_{1} + \rho'_1(\mathcal{G}^{0+}_{00} + \mathcal{G}^{0+}_{0\theta})]\}, \\
M'_{20} &= \sqrt{2}\,(\overline{\mathcal{E}}\,\mathcal{G}^{0+}_{0\theta} + (\overline{\alpha}/\alpha)(z_1/z_2 \rho'_1 \mathcal{G}^{0+}_{1} + \epsilon_2 \mathcal{G}^{0+}_{2})), \\
M'_{30} &= \sqrt{2}\,\{\overline{\mathcal{E}}\,\mathcal{G}^{0+}_{23} + (\overline{\alpha}/\alpha)[\rho_1(\mathcal{G}^{0+}_{0\theta} + \mathcal{G}^{0+}_{1\delta}) + \epsilon_2(\mathcal{G}^{0+}_{0\delta} + \mathcal{G}^{0+}_{3\delta})]\}, \\
M'_{01} &= \sqrt{2}\,(\overline{\alpha}/\alpha)(\rho_1 \mathcal{G}^{0+}_{00} + \rho''_2 \mathcal{G}^{0+}_{0\delta}), \\
M'_{11} &= 1 + (\overline{\alpha}/\alpha)[2\rho_1 \mathcal{G}^{0+}_{0\delta} + \rho''_2(\mathcal{G}^{0+}_{00} + \mathcal{G}^{0+}_{0\theta})], \\
M'_{21} &= (\overline{\alpha}/\alpha)(2\rho_1 \mathcal{G}^{0+}_{0\theta} + \rho''_2 \mathcal{G}^{0+}_{1}), \\
M'_{31} &= (\overline{\alpha}/\alpha)[2\rho_1 \mathcal{G}^{0+}_{23} + \rho''_2(\mathcal{G}^{0+}_{0\theta} + \mathcal{G}^{0+}_{1\delta})], \\
M'_{02} &= \sqrt{2}\,(\overline{\alpha}/\alpha)(\rho_2 \mathcal{G}^{0+}_{00} + \mathcal{J}_1 \sigma_\delta \alpha \mathcal{G}^{0+}_{0\delta}), \\
M'_{12} &= (\overline{\alpha}/\alpha)[2\rho_2 \mathcal{G}^{0+}_{0\delta} + \mathcal{J}_1 \sigma_\delta \alpha(\mathcal{G}^{0+}_{00} + \mathcal{G}^{0+}_{0\theta})], \\
M'_{22} &= 1 + (\overline{\alpha}/\alpha)(2\rho_2 \mathcal{G}^{0+}_{0\theta} + \mathcal{J}_1 \sigma_\delta \alpha \mathcal{G}^{0+}_{1}), \\
M'_{32} &= (\overline{\alpha}/\alpha)[2\rho_2 \mathcal{G}^{0+}_{23} + \mathcal{J}_1 \sigma_\delta \alpha(\mathcal{G}^{0+}_{0\theta} + \mathcal{G}^{0+}_{1\delta})], \\
M'_{03} &= \sqrt{2}\,\overline{\alpha}\,\mathcal{J}_2 \sigma_\delta \mathcal{G}^{0+}_{0\delta}, \\
M'_{13} &= \overline{\alpha}\,\mathcal{J}_2 \sigma_\delta(\mathcal{G}^{0+}_{00} + \mathcal{G}^{0+}_{0\theta}), \\
M'_{23} &= \overline{\alpha}\,\mathcal{J}_2 \sigma_\delta \mathcal{G}^{0+}_{1}, \\
M'_{33} &= 1 + \overline{\alpha}\,\mathcal{J}_2 \sigma_\delta(\mathcal{G}^{0+}_{0\theta} + \mathcal{G}^{0+}_{1\delta}), \\
M'_{44} &= 1 - (\overline{\alpha}/\alpha)\rho''_2(\mathcal{G}^{0+}_{00} - \mathcal{G}^{0+}_{0\theta}), \\
M'_{54} &= -(\overline{\alpha}/\alpha)\rho''_2(\mathcal{G}^{0+}_{0\delta} - \mathcal{G}^{0+}_{23}), \\
M'_{64} &= -(\overline{\alpha}/\alpha)\rho''_2(\mathcal{G}^{0+}_{0\theta} - \mathcal{G}^{0+}_{1\delta}), \\
M'_{45} &= \overline{\alpha}\,\mathcal{J}_1 \sigma_\delta(\mathcal{G}^{0+}_{00} - \mathcal{G}^{0+}_{0\theta}), \\
M'_{55} &= 1 + \overline{\alpha}\,\mathcal{J}_1 \sigma_\delta(\mathcal{G}^{0+}_{0\delta} - \mathcal{G}^{0+}_{23}), \\
M'_{65} &= \overline{\alpha}\,\mathcal{J}_1 \sigma_\delta(\mathcal{G}^{0+}_{0\theta} - \mathcal{G}^{0+}_{1\delta}), \\
M'_{46} &= \overline{\alpha}\,\mathcal{J}_2 \sigma_\delta(\mathcal{G}^{0+}_{00} - \mathcal{G}^{0+}_{0\theta}), \\
M'_{56} &= \overline{\alpha}\,\mathcal{J}_2 \sigma_\delta(\mathcal{G}^{0+}_{0\delta} - \mathcal{G}^{0+}_{23}), \\
M'_{66} &= 1 + \overline{\alpha}\,\mathcal{J}_2 \sigma_\delta(\mathcal{G}^{0+}_{0\theta} - \mathcal{G}^{0+}_{1\delta}).
\end{aligned} \tag{2.17}$$

We have defined the additional parameters $\rho_1 = \mathcal{J}'_1 \alpha_0(1+\sigma_0) - \mathcal{J}_1 \alpha$, $\rho_2 = \mathcal{J}'_2 \alpha_0(1+\sigma_0) - \mathcal{J}_2 \alpha$, $\rho'_1 = \mathcal{J}'_1 \alpha_0(1+\sigma_\delta) - \mathcal{J}_1 \alpha$, $\rho''_2 = \mathcal{J}''_2 \alpha(1+\sigma_\delta) - \mathcal{J}_2 \alpha$, $\overline{\mathcal{E}} = (\mathcal{E}'_0 - \mathcal{E}')/\mathcal{E}\langle S^z\rangle$, $\overline{\alpha} = 8\alpha^2/\mathcal{E}\langle S^z\rangle$. The quantities $\mathcal{G}^{0+}_{0\theta}$, $\mathcal{G}^{0+}_{1}$, and $\mathcal{G}^{0+}_{2}$ can be expressed in terms of $\mathcal{G}^{0+}_{00}$

and $\mathcal{G}_{0\delta}^{0+}$ as follows:

$$\mathcal{G}_{0\theta}^{0+}=(z_1\mathcal{J}_1/z_2\mathcal{J}_2)\{\mathcal{E}[1 - (E-\Delta)\pi\mathcal{G}_{00}^{0+}/\langle S^z\rangle]/8z_1\mathcal{J}_1\alpha^2-\mathcal{G}_{0\delta}^{0+}\},$$

$$\mathcal{G}_1^{0+}=-\mathcal{E}'\mathcal{G}_{00}^{0+}/8\mathcal{J}_2\alpha^2-(\mathcal{J}_1/\mathcal{J}_2)(\mathcal{G}_{00}^{0+}+\mathcal{G}_{0\theta}^{0+}), \quad (2.18)$$

$$\mathcal{G}_2^{0+}=-\mathcal{E}'z_1\mathcal{G}_{0\theta}^{0+}/8z_2\mathcal{J}_2\alpha^2-(z_1\mathcal{J}_1/z_2\mathcal{J}_2)\mathcal{G}_1^{0+}.$$

We see that a quantitative analysis of the results requires numerical calculation of the pure host Green's functions\ $\mathcal{G}_{00}^{0+}$, $\mathcal{G}_{0\delta}^{0+}$, $\mathcal{G}_{23}^{0+}$, $\mathcal{G}_{16}^{0+}$, and $\mathcal{G}_{36}^{0+}$. det $|M'|$ can now be expressed

$$\det|M'|=\det D_s(E)\times\det D_p(E), \quad (2.19)$$

where $D_s(E)$ is the 4×4 matrix in the upper-left-hand corner of (2.16) and $D_p(E)$ is the 3×3 matrix in the lower-right-hand corner. Equating $\det D_s(E)$ to zero determines the four s-type impurity modes; if $\sigma_\delta=0$ only three s modes appear, that is, one new s mode in addition to the two s modes characteristic of nearest-neighbor-only exchange coupling.[3] The p-type modes are determined by $\det D_p(E)=0$. If $\sigma_\delta=0$, then $\rho_2''=\epsilon_2''$, and we get

$$\det D_p(E)=1-(\overline{\alpha}/\alpha)\epsilon_2''(\mathcal{G}_{00}^{0+}-\mathcal{G}_{0\theta}^{0+}), \quad (2.20)$$

the zero of which describes one p-type mode on the sites $\delta=1, 2$. Obviously if we also take $\epsilon_2''=0$ there are no p-type modes. If $\sigma_\delta\neq0$, then all elements in $D_p(E)$ are in general not zero and not unity, so that three p-type modes may appear, each of which are admixtures of the three p-type basis vectors. We discuss the linear chain, and the general case, in more detail in Sec. III.

III. DISCUSSION

The work of Sec. II shows that, when second-nearest-neighbor exchange coupling is considered, several new s-type impurity modes, in addition to those found in I for only nearest-neighbor exchange, may appear in our model. Also, Eq. (2.12) indicates that impurity modes of other symmetries, modes that involve only the neighbors of the impurity and not the impurity itself, may appear only when $\sigma_\delta\neq0$ and/or $\mathcal{J}_2''\neq\mathcal{J}_2$. This is true for a lattice of general symmetry. The results can be explained by invoking a semiclassical picture of precessing pseudospins, similar to that used in Ref. 10 for a fixed spin system. To facilitate the detailed discussion we specify the lattice; the unrealistic case of a linear chain is chosen for simplicity. As shown in equation (2.5), the exchange Hamiltonian involves products of only the x component of pseudospin, in contrast to the dot product of real spin characteristic of the Heisenberg model of an ordinary

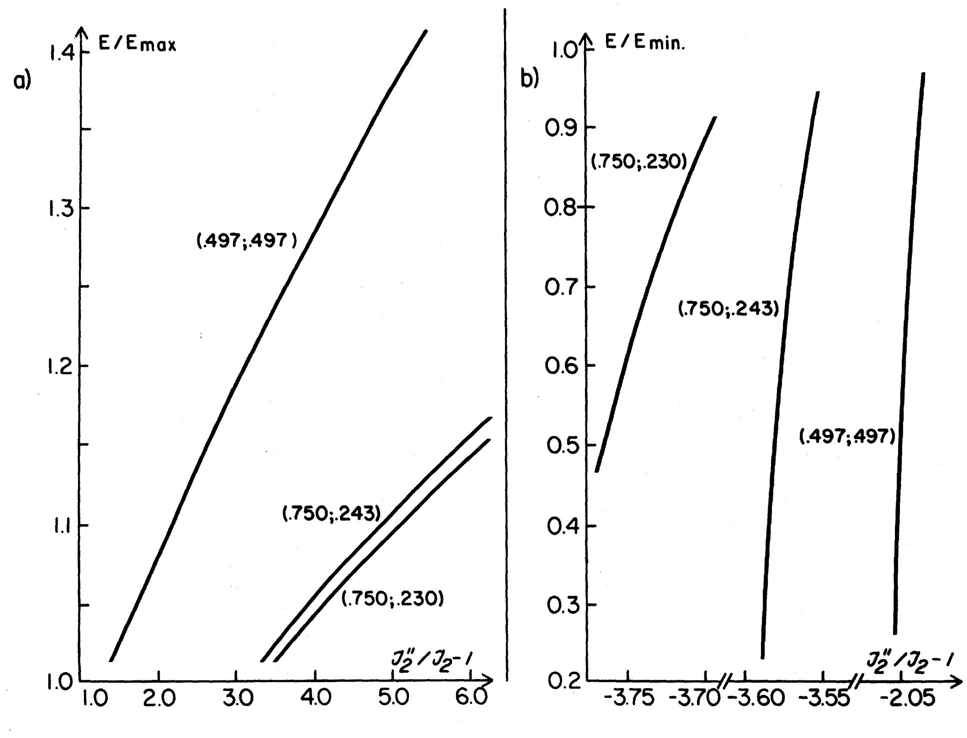

FIG. 1. Energy of local p-type mode in the linear chain lattice, at zero temperature, as a function of parameter $\mathcal{J}_2''/\mathcal{J}_2-1$. The curves are labeled by representative values of the pure crystal parameters $(4z_1\mathcal{J}_1\alpha^2/\Delta,\ 4z_2\mathcal{J}_2\alpha^2/\Delta)$. $\langle S^z\rangle=\langle S_0^z\rangle=\langle S_\delta^z\rangle=\frac{1}{2}$ is taken as an approximation. (a) Local modes above the host band, where $E_{\max}$ is the upper band limit; (b) local modes in the energy gap below the band, where $E_{\min}$ is the lower band limit. The pure crystal Green's functions were calculated numerically using a simple series approximation that is valid only outside the host band.

ordered magnetic system. Consider the $\mathcal{J}_1'$ coupling between the impurity and its nearest neighbors, in the linear chain, for the case $\sigma_6 = 0$. For the p-type motion, the spins at sites 1 and 2 are 180° out of phase with each other and the net precessing field at the impurity site is zero; the impurity then does not participate in the motion, and the ϵ_1-dependent term in the Hamiltonian is zero. Thus in our model we cannot have a p-type impurity mode dependent on ϵ_1. Similar reasoning applies to the exchange coupling $\mathcal{J}_2'$ between the impurity and its second-nearest neighbors. An impurity mode, whose energy must depend on perturbation parameters such as ϵ_1 or ϵ_2, therefore, cannot have p symmetry if only host-impurity exchange is considered. In contrast an s-type mode does depend on these parameters. Now consider the coupling $\mathcal{J}_2''$ between the sites 1 and 2, and the perturbation parameter ϵ_2''. In a p-type mode on these two sites, since the two coupled precessing pseudospins are 180° out of phase, the mode energy is strongly dependent on ϵ_2''. In that case we may have one p-type mode. We now examine $\sigma_6 \neq 0$ (but let $\epsilon_2'' = 0$ for clarity). A p-type mode on the two nearest-neighbor sites can now exist owing to the exchange $\mathcal{J}_2$, since its energy will depend on the quantity σ_6. Two other p-type modes may appear on the pairs of sites 3, 4 (second-nearest neighbors) and 5, 6 (third-nearest neighbors), which are coupled to sites 1, 2 via the couplings $\mathcal{J}_1$ and $\mathcal{J}_2$, respectively, since modes of this type will also depend on σ_6. These three p-type modes all have the same symmetry, so that the resulting three modes will in general be admixtures of the above, as is shown by the appearance of the 3×3 matrix $D_p(E)$ (the four s-type modes will also be admixtures). We also note that all four s-type modes may appear only if $\sigma_6 \neq 0$, even if ϵ_1, ϵ_2, and ϵ_2'' are all nonzero. The energy of an s-type mode on the sites 5, 6 depends on the impurity parameters only through σ_6. The arguments above can easily be extended to other lattices, where, in addition to p-type modes, d, f, etc. may appear, but only if $\epsilon_2'' \neq 0$ and/or $\sigma_6 \neq 0$.

The modes, when they exist, can be either local or resonance modes, depending on the values of the various perturbation parameters. Local modes, which may appear above the host band and/or in the energy gap below the band, are in general easier to detect and measure. Experimentally one can usually detect the number of modes and their energies and symmetries, even in those cases where the large number of parameters and/or lack of a suitable model for the given system make a more detailed interpretation of the results difficult. In this way useful information may be obtained about the system even in adverse situations. As an example, suppose a p-type local mode were detected. σ_6, which is not an adjustable parameter but is a self-consistently determined quantity depending on other perturbation parameters, will in general not be expected to be large enough to cause, by itself, an impurity mode to become localized. In contrast the parameter ϵ_2'' can, in principle, be large, so that the local mode would be due to a large difference between $\mathcal{J}_2''$ and $\mathcal{J}_2$. Figure 1 shows the energy of a local p-type mode in the linear chain lattice as a function of $\mathcal{J}_2''/\mathcal{J}_2 - 1$, for zero temperature in the approximation $\langle S^z\rangle = \langle S_0^z\rangle = \langle S_\delta^z\rangle = \frac{1}{2}$. Modes both above the host band and in the gap below the band are shown. We recall that $\mathcal{J}_2''$ couples two host ions in the vicinity of the impurity; therefore the detection of the p mode may give information about the mechanism, or the relative importance of various mechanisms, of exchange couplings in the crystal. If the coupling is of the RKKY type, as in the rare-earth metals, we would not expect ϵ_2'' to be as large as it may be if superexchange via the impurity site (or via ligand ions near the impurity, where the outer electron wave functions can be greatly altered owing to the presence of the impurity) is the important mechanism. The detection of the local p-type mode would favor the superexchange model.

We have discussed in detail only exchange coupling to second-nearest neighbors. The qualitative arguments can be extended to further-neighbor coupling, as can be most easily seen in the semiclassical picture discussed above. In conclusion we comment that the results of this paper may be valid only for small impurity concentrations, where only effects linear in the concentration are important. At somewhat larger concentrations, pair effects become important. These effects need to be considered on their own merit; for example, a p mode depending on impurity-impurity coupling appears for impurities that are themselves nearest neighbors,[11,12] and this p mode has nonzero amplitude on the impurity sites.

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Hyperfine-Enhanced Magnetic Ordering in Singlet-Ground-State Systems*

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It is shown that in systems with single-electronic ground states the simultaneous diagonalization of a hyperfine, as well as an exchange interaction, gives rise to an interference between these two effects which has important consequences on the properties of such a system. It is found, for example, that long-range order is now possible for values of the exchange below that previously thought necessary. Calculations are presented for the magnetic moment, heat capacity, susceptibility, and collective modes for a system involving praseodymium.

Considerable attention[1] has recently been given to rare-earth systems whose electronic ground states are singlets. There are a variety of reasons for such interest, including the successful demagnetization[2] of hyperfine-enhanced nuclear systems, the appearance[3-7] of electronic ordering above a critical value for the exchange interaction, and the possibility[2,8] of observing cooperative nuclear ordering in systems with exchange interactions less than this critical value. Furthermore, inelastic-neutron-scattering experiments suggest that the ordering in fcc Pr[9] and Pr_3Tl,[9] and possibly dhcp Pr,[10,11] does not exhibit the expected soft-mode behavior.

Recently, Katila *et al.*[7] have reported calculations on an electronically ordered singlet-ground-state system within the molecular-field approximation (MFA) including the magnetic hyperfine interaction which show a surprisingly large hyperfine enhancement of the electronic moment at low temperatures. Since crystal-field effects which tend to destroy the ionic moment are comparable in size with the exchange forces which have the opposite effect, the calculation in Ref. 7 suggests that the hyperfine interaction may play a crucial role in determining the magnetic properties of these systems. We report here an investigation of the properties of such systems, including the heat capacity, the magnetic susceptibility, and collective modes. In particular, it will be shown that the hyperfine interaction can induce long-range order even when the exchange interaction between ions is well below the critical value generally considered necessary for such ordering. Furthermore, under certain conditions the temperature at which ordering occurs is much higher than that associated with indirect nuclear coupling, a result that has recently been observed in $PrCu_2$.[8]

Let us consider a system characterized by the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{\text{crystal field}} + \mathcal{H}_{\text{exch}} + \sum_i (\mathcal{A}\vec{I}_i \cdot \vec{J}_i + g_J \mu_B \vec{H} \cdot \vec{J}_i + g_N \mu_N \vec{H} \cdot \vec{I}_i) \ , \qquad (1)$$

where the terms in the summation are the hyperfine interaction and the electronic and nuclear Zeeman terms, respectively. We shall assume that the crystal-field states consist of two low-lying singlets separated by Δ. For the moment, we shall also assume $I = \frac{1}{2}$, so that the unperturbed nuclear eigenstates are $|\pm\frac{1}{2}\rangle$. Our basis states, therefore, consist of the four products of the crystal-field states, and these nuclear states which we shall write as $|\gamma, m\rangle$. We shall also adopt the usual assumption in the induced-moment problem that we can define our coordinate system such that the matrix elements of $\vec{J}$ have the form

$$\langle \gamma, m | J_\mu | \gamma', m' \rangle = \alpha \delta_{\mu, z} (1 - \delta_{\gamma\gamma'}) \delta_{m, m'} \qquad (2)$$

and that the magnetic field can, in fact, be applied along this z axis.

It is convenient to introduce the following parameters:

$$\eta = \frac{4\mathcal{J}(0)\alpha^2}{\Delta} \ , \quad x = \frac{\eta \langle J_z \rangle}{\alpha} \ , \quad b = \frac{2\mathcal{A}\alpha}{\Delta} |m|$$
$$c = \frac{g_N \mu_N H}{\Delta} \ , \quad d = \frac{2 g_J \mu_B \alpha H}{\Delta} \ . \qquad (3)$$

If we apply the molecular-field approximation to the exchange interaction, the resulting 4×4 matrix