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THEORY OF SINGLET-DOUBLET EXCITATIONS IN PRASEODYMIUM*

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ABSTRACT

The magnetic excitation spectrum in a paramagnetic singlet-doublet system is calculated using a diagrammatic high density expansion technique. The lowest order diagrams, which correspond to the random phase approximation (RPA), give a detailed description of the wavevector and temperature dependence of the four exciton modes in Praseodymium in terms of a Hamiltonian including isotropic Heisenberg exchange interactions and anisotropic, dipolar-like interactions. The leading contributions to the linewidths of the excitations are obtained by extending the $1/Z$ expansion of the generalised susceptibility propagators one order beyond the random phase approximation. This damping corresponds to spin wave scattering on single-site fluctuations. The theoretical spectral functions are in detailed agreement with experiment.

I. INTRODUCTION

For the last several years there has been a great interest in the properties of localized magnetic systems which possess a nonmagnetic singlet ground state.¹ The ordering in such systems occurs as an exchange polarization of the ground state, provided the exchange interaction between the magnetic ions exceeds a certain threshold value.

Most of the theoretical work on singlet-ground state systems has been based on the random phase approximation (RPA) using a variety of different representations of the single-ion states, or on pseudoboson theories which essentially give the zero temperature limit of the RPA. More elaborate theories based on various higher-order decouplings of equations of motions of spin operators give corrections to the exciton energies. However, inconsistencies and ambiguities are introduced through the decoupling procedures and it is difficult to estimate the errors introduced via the truncations. Another shortcoming of most of these theories is that they give infinite lifetimes of the excitations and thus completely neglect damping effects. An alternative type of theory is the diagrammatic Green's function expansion method developed by Vaks, Larkin and Pikin (VLP) for spin-operators to calculate correlation functions to any order of perturbation theory.² The formalism has later been generalized by Kashchenko *et al.*³ and by Izyumov and Kassin-Ogly.⁴ Yang and Wang⁵ extended the method to any multilevel magnetic system using a standard basis operator

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representation. The VLP formalism corresponds to the semi-invariant theory introduced by Stinchcombe *et al.* which has been applied to the Ising model in a transverse field.⁶ In contrast to the other techniques, this kind of theory gives a well defined high-density expansion parameter $(1/2)$ or $(1/r_0^3)$, allowing us to perform systematic selfconsistent calculations, and to recognize the physical processes involved. The approximations are based on physical, not technical reasons. Praseodymium is an example of a singlet ground state magnet in which the exchange is only slightly undercritical with respect to magnetic ordering. The ground state on the hexagonal sites is the pure $|J^z = 0\rangle$ singlet, and the first excited state is the doublet $|x\rangle, |y\rangle$, where $|x\rangle = 1/\sqrt{2} (|1\rangle + |-1\rangle)$ and $|y\rangle = -i/\sqrt{2} (|1\rangle - |-1\rangle)$. The paramagnetic excitation spectrum has recently been measured by Houmann *et al.*⁷ using inelastic neutron scattering technique. The temperature dependence of the excitation energies were found to be in substantial agreement with a random phase theory (RPA), and the lowest lying mode shows a clear tendency towards softening as the temperature is lowered towards 0 K. In addition to strong temperature dependence of the exciton energies, a dramatic increase of the intrinsic linewidth was observed as the temperature was raised from 6 K to 30 K, where well-defined modes cease to exist. dhcp Praseodymium seems to be the simplest real singlet-ground-state magnet, and significantly more information is now available on the excitations in this material than in any other paramagnetic system. This makes the element Pr almost ideal for a confrontation between experiment and theoretical model calculations.

GREEN'S FUNCTION FORMALISM AND RPA THEORY

The effective Hamiltonian describing the magnetic ions on the hexagonal sites in Pr may be written

$$H = \sum_i \Delta (S_i^z)^2 - \sum_{ij, \alpha\beta} J_{ij}^{\alpha\beta} S_i^\alpha S_j^\beta, \quad \alpha, \beta = x, y \quad (1)$$

Δ is the crystal field splitting ($= 3.2 \text{ MeV}^7$). We introduce the Green's functions

$$G^{\alpha\beta}(r_1, \tau_1; r_2, \tau_2) = \langle T_\tau S^\alpha(r_1, \tau_1) S^\beta(r_2, \tau_2) \rangle, \quad (2)$$

where $\langle T_\tau \dots \rangle$ denotes the thermal average of the τ ordered product of operators in the interaction represen-

tation. The Green's functions are calculated for $\alpha, \beta = x, y$ only. It is a standard procedure to expand the Green's functions in the form

$$G^{\alpha\beta}(\vec{r}_1, \tau_1; \vec{r}_2, \tau_2) = \langle T_\tau S^\alpha(\vec{r}_1, \tau_1) S^\beta(\vec{r}_2, \tau_2) \mathcal{L}(\beta) \rangle_0 / \langle \mathcal{L}(\beta) \rangle_0$$

$$\mathcal{L}(\beta) = T_\tau \exp \left(- \int_0^\beta \mathcal{H}_{int}(\tau) d\tau \right) \quad (3)$$

where the averages are taken with respect to the single-ion part of the Hamiltonian.

In general, this expansion can be represented by a sum of connected diagrams representing an aggregate of single-cell blocks joined by interaction lines. The non-interacting Green's functions, $g_0(i\omega_n) = 2\Delta(\Delta^2 - i\omega_n)^2)^{-1}$, are represented by full lines, and the interactions by wavy lines. ω_n are the Matsubara frequencies. The propagators $G^{\alpha\beta}(\vec{q}, i\omega_n)$ are represented by double lines. The single-cell blocks are surrounded by broken lines to denote that the propagators involved are restricted to the same site. A diagram containing N independent wavevector labels, which are eventually summed over, is of order $(1/2)^N$. The zeroth order diagrams simply consist of non-interacting Green's function connected with interaction lines (see the RPA-diagrams in Fig. 2a). The poles of the RPA-propagators, which give the energy spectrum are⁹

$$(\omega_{\vec{q}}^N)^2 = \Delta^2 - 4\Delta R J^N(\vec{q}) \quad (4)$$

where $R = \{1 - \exp(-\beta\Delta)\} \{1 + 2\exp(-\beta\Delta)\}^{-1}$ and $J^N(\vec{q})$ are eigenvalues of a 4×4 matrix describing the exchange interactions between the ions. The measured dispersion relations were fitted to this expression (see Fig. 1) and interatomic exchange parameters were derived. The polarisations of the exciton modes are in general elliptic or linear, and the polarisation vector changes rapidly as a function of $\vec{q}$, in particular at large wavevectors.

The RPA theory has thus allowed us to set up a theory of the dispersion relations, and to construct a complete model to describe the magnetic properties of the hexagonal ions, and we can now calculate higher order diagrams without introducing any adjustable parameters.

FLUCTUATION DAMPING OF EXCITATIONS

To find the first order corrections to the Green's functions we collect all the single-cell blocks with one interaction-loop. The real part of these diagrams give rise to a small shift of the excitation energies.¹⁰ It turns out, however, that only the diagram in Fig. 2b gives a contribution to the damping of the excitations. The imaginary part, which is of interest here, has the following analytic expression in $\omega_{\vec{q}}$ space:

$$G_1(i\omega_n) = 2g_0(i\omega_n)^2 b i \operatorname{Im} \frac{1}{N} \sum_{\vec{q}'} \mathcal{J}_S(\vec{q}', i\omega_n) \quad (5)$$

where $b = \{5\exp(-\beta\Delta) + \exp(-2\beta\Delta)\} [1 + 2\exp(-\beta\Delta)]^{-2}$. The diagram corresponds to scattering of excitation waves on single-site fluctuations of the population difference (or quadrupole moment) R . The intermediate states are magnetic excitations with wavevector $\vec{q}'$. This effect corresponds to scattering of spinwaves on fluctuations of $\langle S_z^2 \rangle$ for a simple ideal ferromagnet as discussed by Vaks et al.² It is interesting that the damping occurs to first order in the expansion. For boson or fermion systems, the lowest order imaginary part of the self energy occurs in second order in the high density expansion due to interaction between excitations. The resulting Green's functions including all chain diagrams involving $G_0(i\omega_n)$ and $G_1(i\omega_n)$ are

$$G^N(\vec{q}, i\omega_n) = [G_0(i\omega_n) + G_1(i\omega_n)] [1 - 2\mathcal{J}^N(\vec{q}) (G_0(i\omega_n) + G_1(i\omega_n))]^{-1} \quad (6)$$

The spectral functions, which are proportional to the neutron scattering cross-section, can easily be expressed in terms of the Green's functions using the fluctuation-dissipation theorem:

$$\begin{aligned} S^N(\vec{q}, \omega) &= \frac{1}{\pi} [1 - \exp(-\beta\omega)]^{-1} \operatorname{Im} G^N(\vec{q}, \omega) \\ &= \frac{1}{\pi} [1 - \exp(-\beta\omega)]^{-1} \frac{\gamma(\omega) (\Delta^2 - \omega^2)}{((\omega_{\vec{q}}^N)^2 - \omega^2)^2 + (2\gamma(\omega) \mathcal{J}^N(\vec{q}))^2} \end{aligned} \quad (7)$$

where the damping parameter $\gamma(\omega)$ must be determined self-consistently by solving the integral equation

$$\begin{aligned} \gamma(\omega) &= (\Delta^2 - \omega^2) \operatorname{Im} G_1(\omega) \\ &= 16\Delta^2 b \int_{\omega'} d\omega' \frac{\left(\frac{1}{4} \sum_N N_T^N(\omega')^2 \mathcal{J}^2(\omega') \gamma(\omega') \right)}{(\omega'^2 - \omega^2)^2 + (2\gamma(\omega) \mathcal{J}(\omega'))^2} \end{aligned} \quad (8)$$

The summation over $\vec{q}'$ space has been changed to an integration over ω' space. $N_T^N(\omega)$ is the density of states for the N 'th excitation mode at temperature T , and $\mathcal{J}(\omega')$ is the value of $\mathcal{J}^N(\vec{q}')$ for a mode with energy ω' determined by (4). The theoretical lineshapes convoluted with the experimental resolution function are compared with experiment in Fig. 3. Almost complete agreement between positions of peaks, intensities and lineshapes is observed at any temperature. The agreement is least perfect at the highest temperatures, where the linewidth, as calculated

to first order in the $(1/Z)$ expansion, is comparable to the energy as calculated to zeroth order. Hence, damping effects due to other effects, such as interactions between excitations occurring to order $(1/Z)^2$ in the expansion, scattering on phonons, or direct Coulomb scattering with conduction electrons, can be entirely neglected at least at moderate temperatures. This fundamental understanding of the excitations in Pr may be valuable for the understanding not only of other singlet ground state systems of magnetic or non-magnetic nature, such as the hydrogen bonded ferroelectrics, but also of more complicated systems, since the formalism can easily be extended to arbitrary level schemes.

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FIGURE CAPTIONS

Fig. 1 Dispersion relations for magnetic excitations propagating on the hexagonal sites in dhcp Praseodymium. The experimental data is taken from Ref. 7. The full lines represent a least squares fit as described in the text.

Neg. #5-252-75

Fig. 2 a) RPA diagram representing the zeroth order term in the $(1/Z)$ expansion. b) First order single-cell block representing fluctuation scattering of excitons. c) "Screened" interaction.

Neg. #5-249-75

Fig. 3 Spectral functions for magnetic excitations in Pr. Points: neutron measurements (Ref. 11), lines: selfconsistently calculated lineshapes convoluted with the experimental resolution (Gaussian, full width at half maximum = 0.36 meV).

Neg. #3-320-75

$$\overline{G}(\vec{q}, i\omega_n) = \frac{\overline{G}_0(i\omega_n)}{2\overline{G}_0(i\omega_n)} + \frac{\overline{G}_0(i\omega_n)}{2\overline{G}_0(i\omega_n)} \overline{G}(\vec{q}, i\omega_n)$$

$$G_1(i\omega_n) =$$

$$f_s^{\alpha\alpha}(\vec{q}, i\omega_n) = \text{diagram 1} + \text{diagram 2}$$