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Spin fluctuations in a spin-1 paramagnet with easy-planar anisotropy: Application to praseodymium

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Abstract. The effects of fluctuations in an $S = 1$ Heisenberg system with strong easy-planar crystal-field anisotropy are considered in the paramagnetic phase. The Green functions are derived from their equations of motion. The decoupling procedure properly accounts for single-site correlation. The spin-correlation functions are determined self-consistently by equations which reduce to the ones derived in the correlated-effective-field approximation of M E Lines in the limits of high temperatures or small anisotropy. The linewidths deduced for the magnetic excitations compare with the results of Bak, determined by a diagrammatic expansion of the Green functions to first order in $1/Z$. Except for the introduction of the finite lifetime of the excitations, the application of the theory to the case of Pr leads to only minor adjustment of the 'effective' molecular-field properties.

1. Introduction

The magnetic properties of DHCP (double hexagonal close-packed) Pr have been studied in great detail (Houmann *et al* 1979, Jensen 1979). The magnetic behaviour is dominated by the ions on the hexagonal sites in the Pr lattice. The ground state of these ions is the singlet $|0\rangle$ state (z is along the c axis) and the lowest excited state is the $|\pm 1\rangle$ doublet. This arrangement of the crystal-field levels implies that the low-temperature properties of the hexagonal ions correspond to the spin-1 case, even though $J = 4$ for the tripositive Pr ions.

Pr is a singlet-ground-state system for which the two-ion coupling is just below the critical value. In fact, an antiferromagnetic ordering takes place in the millikelvin range, where the nuclear spins become important (McEwen and Stirling 1981) or between 5–15 K when the crystal is subjected to a moderate uniaxial stress (McEwen *et al* 1978). Later and more extensive measurements of T_N as a function of the uniaxial stress (K A McEwen, private communication) suggest that the exchange coupling is about 0.96 times the critical value, which is closer to 1 than the previous estimate of 0.92 (see Houmann *et al* 1979). Pr is thus very close to ordering magnetically in its electronic regime above 1 K, where the nuclear spins can be neglected. This suggests that spin correlation should be included in a description of the low-temperature properties of Pr. This point of view is substantiated by the observation of a central peak in the neutron-scattering response below 10 K and close to the wavevector characterising the ordered phase (Houmann *et al* 1977, McEwen *et al* 1978, McEwen and Stirling 1981).

Motivated by these considerations we analyse in § 2 the spin-fluctuations in an

$S = 1$ Heisenberg paramagnet in the presence of easy-planar single-ion anisotropy. The opposite case of easy-axis anisotropy has been treated by Yang and Wang (1975). Bak (1975a, b) considered the effect of spin fluctuations on the damping of the magnetic excitons in the easy-planar case.

In § 3 the theory is applied to the case of Pr. The self-consistent correlation effects are determined numerically, and comparisons with experiments are given. Finally, we discuss in § 4 the success and shortcomings of the present theory in its application to Pr.

2. Spin fluctuations in an $S = 1$ system

The Hamiltonian of the system is taken as

$$\mathcal{H} = \Delta_0 \sum_i (S_i^z)^2 - \tfrac{1}{2} \sum_{i,j} \mathcal{J}(ij)\, \mathbf{S}_i \cdot \mathbf{S}_j \tag{1a}$$

with $S = 1$ and Δ_0 positive, and it is assumed to be in the paramagnetic state. First we introduce the standard basis operators (Haley and Erdös 1972, see also Yang and Wang 1975) for the ith ion:

$$a^i_{\mu\nu} = (|\mu\rangle\langle\nu|)_i, \qquad \mu, \nu = 0, 1, 2$$

taking the single-spin (molecular-field) eigenstates as the basis: $|1\rangle = 2^{-1/2}\,(|+1\rangle + |-1\rangle)$ and $|2\rangle = (-2)^{-1/2}\,(|+1\rangle - |-1\rangle)$. In terms of these operators the Hamiltonian can be written:

$$\begin{aligned}\mathcal{H} = \Delta_0 \sum_i (a^i_{11} + a^i_{22}) - \tfrac{1}{2} \sum_{i,j} [&\mathcal{J}_1(ij)(a^i_{01} + a^i_{10})(a^j_{01} + a^j_{10}) \\ &+ \mathcal{J}_2(ij)(a^i_{02} + a^i_{20})(a^j_{02} + a^j_{20}) - \mathcal{J}_3(ij)(a^i_{12} - a^i_{21})(a^j_{12} - a^j_{21})]\end{aligned} \tag{1b}$$

with

$$\mathcal{J}_1(ij) = |\langle 0|\, S^x\, |1\rangle|^2\, \mathcal{J}(ij),$$

$$\mathcal{J}_2(ij) = |\langle 0|\, S^y\, |2\rangle|^2\, \mathcal{J}(ij),$$

and

$$\mathcal{J}_3(ij) = |\langle 1|\, S^z\, |2\rangle|^2\, \mathcal{J}(ij).$$

If $S = 1$, all the squared matrix elements are equal to 1, whereas in Pr($S = 4$)

$$\mathcal{J}_1(ij) = \mathcal{J}_2(ij) = 10\, \mathcal{J}_3(ij) = 10\, \mathcal{J}(ij).$$

In order to be able to generalise the results to the case of Pr we shall differentiate between the three cartesian components. Further, we introduce the simplification that $\mathcal{J}_3(ij) = 0$, and discuss this term separately later.

The retarded double-time Green functions are defined (Zubarev 1960) in the form of a 2×2 matrix:

$$\tilde{G}(ij, t) = -\mathrm{i}\theta(t) \begin{pmatrix} \langle [a^i_{01}(t), a^j_{10}(0)] \rangle & \langle [a^i_{01}(t), a^j_{01}(0)] \rangle \\ \langle [a^i_{10}(t), a^j_{10}(0)] \rangle & \langle [a^i_{10}(t), a^j_{01}(0)] \rangle \end{pmatrix}. \tag{2a}$$

Introducing the Fourier transforms of $\tilde{G}(ij, t)$ with respect to the space and the time variables

$$\tilde{G}(\boldsymbol{q}, \omega) = \frac{1}{N}\sum_{i,j} \exp(-\mathrm{i}\boldsymbol{q} \,.\, \boldsymbol{R}_{ij}) \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{e}^{\mathrm{i}\omega t} \tilde{G}(ij, t) \tag{2b}$$

then the generalised susceptibility $\chi_1(\boldsymbol{q}, \omega)$ (the xx component in units of $\frac{1}{3}S(S+1)(g\mu_B)^2$) is

$$\chi_1(\boldsymbol{q}, \omega) = -\sum_{\alpha,\beta=1,2} G_{\alpha\beta}(\boldsymbol{q}, \omega). \tag{3}$$

The equations of motion of the Green functions are derived using the commutator relation:

$$[a^i_{\mu\nu}, a^j_{\mu'\nu'}] = \delta_{ij}(\delta_{\nu\mu'} \, a^i_{\mu\nu'} - \delta_{\mu\nu'} \, a^i_{\mu'\nu}). \tag{4}$$

Introducing the double-bracket notation for the higher-order Green functions we obtain ($\alpha = 1$ or 2):

$$\begin{aligned}(\Delta_0 - \omega) \, G_{1\alpha}(\boldsymbol{q}, \omega) &- n_{01} \, \mathcal{J}_1(\boldsymbol{q})(G_{1\alpha}(\boldsymbol{q}, \omega) + G_{2\alpha}(\boldsymbol{q}, \omega)) \\ &- \frac{1}{N}\sum_{ijj'} [\mathcal{J}_1(ij) \, \langle\langle (a^i_{00} - a^i_{11} - n_{01})(a^j_{01} + a^j_{10}) \, ; a^{j'}_{\alpha} \rangle\rangle \\ &- \mathcal{J}_2(ij) \, \langle\langle a^i_{21}(a^j_{02} + a^j_{20}) \, ; a^{j'}_{\alpha} \rangle\rangle] \exp(-\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{R}_{ij'}) \\ = -n_{01}\delta_{\alpha,1}\end{aligned} \tag{5}$$

where $a^{j'}_1$ and $a^{j'}_2$ mean $a^{j'}_{10}$ and $n^{j'}_{01}$ respectively, and $n_{01} \equiv n_0 - n_1$ is the thermal expectation value $\langle a^i_{00} \rangle - \langle a^i_{11} \rangle$. In the random-phase approximation (RPA) the higher-order Green functions $\langle\langle a^i_{\mu\nu} a^j_{\mu'\nu'} \, ; a^{j'}_{\mu''\nu''} \rangle\rangle_{i \neq j}$ are replaced by

$$\langle a^i_{\mu\nu} \rangle \, \langle\langle a^j_{\mu'\nu'} \, ; a^{j'}_{\mu''\nu''} \rangle\rangle + \langle a^j_{\mu'\nu'} \rangle \, \langle\langle a^i_{\mu\nu} ; a^{j'}_{\mu''\nu''} \rangle\rangle.$$

In this approximation the terms in the square bracket of (5) are neglected and the result is

$$\tilde{G}(\boldsymbol{q}, \omega) = -\frac{n_{01}}{D_q^2 - \omega^2}\begin{pmatrix} \Delta - \xi_q + \omega & \xi_q \\ \xi_q & \Delta - \xi_q - \omega \end{pmatrix}. \tag{6a}$$

D_q is the excitation energy at wavevector $\boldsymbol{q}$:

$$D_q^2 = \Delta^2 - 2\Delta\xi_q \tag{6b}$$

where in the RPA:

$$\Delta = \Delta_0 \qquad \xi_q = n_{01} \, \mathcal{J}_1(\boldsymbol{q}). \tag{6c}$$

The following matrix of equal-time correlation functions:

$$\tilde{A}_q = \frac{1}{N}\sum_{i,j} \exp(-\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{R}_{ij})\begin{pmatrix} \langle a^i_{01} \, a^j_{10} \rangle & \langle a^i_{01} \, a^j_{01} \rangle \\ \langle a^i_{10} \, a^j_{10} \rangle & \langle a^i_{10} \, a^j_{01} \rangle \end{pmatrix} \tag{7}$$

should according to the fluctuation-dissipation theorem be related to $\tilde{G}(\boldsymbol{q}, \omega)$:

$$\tilde{A}_q = -\frac{1}{\pi}\int_{-\infty}^{\infty} \mathrm{d}\omega \frac{1}{1 - \mathrm{e}^{-\beta\omega}} \tilde{G}''(\boldsymbol{q}, \omega) \tag{8}$$

where $\beta = 1/k_B T$, or

$$\tilde{A}_q = \frac{n_{01}}{2D_q}\begin{pmatrix} (\Delta - \xi_q)\eta_q + D_q & \xi_q\eta_q \\ \xi_q\eta_q & (\Delta - \xi_q)\eta_q - D_q \end{pmatrix} \tag{9a}$$

where

$$\eta_q = \coth(\beta D_q/2). \tag{9b}$$

These correlation functions should satisfy a number of relations, for instance

$$A_q^{11} - A_q^{22} = n_{01} \tag{10}$$

according to the equations (4) and (7). By definition (equation (7))

$$\frac{1}{N}\sum_q (A_q^{11} + A_q^{22}) = \langle a_{01}^i a_{10}^i\rangle + \langle a_{10}^i a_{01}^i\rangle = n_0 + n_1$$

and

$$\frac{1}{N}\sum_q A_q^{12} = \frac{1}{N}\sum_q A_q^{21} = \langle a_{01}^i a_{01}^i\rangle \equiv 0$$

which imply the following relations

$$\frac{1}{N}\sum_q \frac{\Delta - \xi_q}{D_q}\eta_q = \frac{n_0 + n_1}{n_{01}} \tag{11}$$

and

$$\frac{1}{N}\sum_q \frac{\xi_q}{D_q}\eta_q = 0. \tag{12}$$

In RPA (10) is fulfilled; however, (12) is in general violated to second order in $\mathcal{J}_1(\boldsymbol{q})/\Delta_0$ (using the relation $(1/N)\ \Sigma_q \mathcal{J}_1(\boldsymbol{q}) \equiv 0$). This means that different combinations of correlation functions lead to different results for the single-ion averages, and (11) is only useable to zero order in $\mathcal{J}_1(\boldsymbol{q})/\Delta_0$, in which order it reduces to the molecular-field expression. This inconsistency of the RPA method is discussed further by Yang and Wang (1975). In order to eliminate this arbitrariness we have to include effects due to the higher-order Green functions in (5).

We shall illustrate the method by deriving the equation of motion for the Green function:

$$F_{1\alpha}(\boldsymbol{q}, \boldsymbol{k}, \omega) = \frac{1}{N}\sum_{ijj''} \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_{ij''})\exp(-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{R}_{ij})$$
$$\times \langle\langle (1 - \delta_{ij})(a_{00}^i - a_{11}^i - n_{01})a_{01}^j ; a_\alpha^{j''}\rangle\rangle \tag{13}$$

and $F_{2\alpha}(\boldsymbol{q}, \boldsymbol{k}, \omega)$ where a_{10}^j replaces a_{01}^j. First, we consider the commutator:

$$[(1 - \delta_{ij})(a_{00}^i - a_{11}^i - n_{01})a_{01}^j, \mathcal{H}] = \Delta_0(1 - \delta_{ij})(a_{00}^i - a_{11}^i - n_{01})a_{01}^j$$
$$- \sum_{j'} (1 - \delta_{ij})[\mathcal{J}_1(jj')(a_{00}^i - a_{11}^i - n_{01})(a_{00}^j - a_{11}^j)(a_{01}^{j'} + a_{10}^{j'})$$
$$+ 2\mathcal{J}_1(ij')(a_{01}^i - a_{10}^i)(a_{01}^{j'} + a_{10}^{j'})a_{01}^j - \mathcal{J}_2(jj')(a_{00}^i - a_{11}^i - n_{01})a_{21}^j(a_{02}^{j'} + a_{20}^{j'})$$
$$+ \mathcal{J}_2(ij')(a_{02}^i - a_{20}^i)(a_{02}^{j'} + a_{20}^{j'})a_{01}^j]$$

$$\begin{aligned}
&\approx \Delta_0(1-\delta_{ij})(a^i_{00}-a^i_{11}-n_{01})a^j_{01}\\
&\quad -\sum_{j'}\mathcal{J}_1(jj')n_{01}(1-\delta_{ij'})(a^i_{00}-a^i_{11}-n_{01})(a^{j'}_{01}+a^{j'}_{10})\\
&\quad -\mathcal{J}_1(ij)[(n_0+n_1-n^2_{01})a^j_{01}-(n_0+n_1+n^2_{01})a^i_{10}]\\
&\quad -\sum_{j'}2\mathcal{J}_1(ij')[\langle a^i_{01}a^j_{01}-a^i_{10}a^j_{01}\rangle(1-\delta_{ij})(a^{j'}_{01}+a^{j'}_{10})\\
&\quad +\langle a^{j'}_{01}a^j_{01}+a^{j'}_{10}a^j_{01}\rangle(1-\delta_{jj'})(a^i_{01}-a^i_{10})]. \qquad (14)
\end{aligned}$$

When j' is equal to i or j in the exact commutator the triple-product operators truncate into two operators. For other values of j' the triple-products are reduced by an RPA (or Hartree–Fock) decoupling. Further, we neglect terms like

$$\mathcal{J}_1(ij)(a^j_{00}-a^j_{11}-n_{01})a^i_{01}$$

or

$$\mathcal{J}_2(ij)a^i_{02}a^j_{21}$$

which are off-diagonal in Fourier space, and therefore are higher-order corrections. With the approximate commutator relation, the equation of motion becomes:

$$\begin{aligned}
&(\Delta_0-\omega)\,F_{1\alpha}(\boldsymbol{q},\boldsymbol{k},\omega)-n_{01}\,\mathcal{J}_1(\boldsymbol{k})\{F_{1\alpha}(\boldsymbol{q},\boldsymbol{k},\omega)+F_{2\alpha}(\boldsymbol{q},\boldsymbol{k},\omega)\}\\
&\qquad =K^a_\alpha(\boldsymbol{q},\boldsymbol{k},\omega)+K^b_\alpha(\boldsymbol{q},\boldsymbol{k},\omega) \qquad (15)
\end{aligned}$$

where

$$\begin{aligned}
K^a_\alpha(\boldsymbol{q},\boldsymbol{k},\omega)&=-[A^{12}_{\boldsymbol{k}}-(A^{11}_{\boldsymbol{k}}-n_0)]+\{2\mathcal{J}_1(\boldsymbol{q})[A^{12}_{\boldsymbol{k}}-(A^{11}_{\boldsymbol{k}}-n_0)]-n^2_{01}\,\mathcal{J}_1(\boldsymbol{k})\}\\
&\quad\times[G_{1\alpha}(\boldsymbol{q},\omega)+G_{2\alpha}(\boldsymbol{q},\omega)] \qquad (16a)
\end{aligned}$$

and

$$\begin{aligned}
K^b_\alpha(\boldsymbol{q},\boldsymbol{k},\omega)&=(A^{12}_{\boldsymbol{k}}+A^{11}_{\boldsymbol{k}}-n_0)(\delta_{\alpha,1}-\delta_{\alpha.2})+\mathcal{J}_1(\boldsymbol{k})[n_0+n_1+2(A^{12}_{\boldsymbol{k}}+A^{11}_{\boldsymbol{k}}-n_0)]\\
&\quad\times[G_{1\alpha}(\boldsymbol{q},\omega)-G_{2\alpha}(\boldsymbol{q},\omega)] \qquad (16b)
\end{aligned}$$

and equivalently with 1α and 2α interchanged and $\Delta_0-\omega$ replaced by $\Delta_0+\omega$. The first term in the square bracket of (5) is then found to be:

$$\begin{aligned}
&\frac{1}{N}\sum_{\boldsymbol{k}}\mathcal{J}_1(\boldsymbol{k})[F_{1\alpha}(\boldsymbol{q},\boldsymbol{k},\omega)+F_{2\alpha}(\boldsymbol{q},\boldsymbol{k},\omega)]\\
&\qquad =\frac{1}{N}\sum_{\boldsymbol{k}}\mathcal{J}_1(\boldsymbol{k})\frac{1}{n_{01}}\chi_1(\boldsymbol{k},\omega)\left(K^a_\alpha(\boldsymbol{q},\boldsymbol{k},\omega)+\frac{\omega}{\Delta_0}K^b_\alpha(\boldsymbol{q},\boldsymbol{k},\omega)\right). \qquad (17)
\end{aligned}$$

Following the same procedure we get for the second term in the square bracket of (5):

$$\begin{aligned}
&\frac{1}{N}\sum_{ijj'}[-\mathcal{J}_2(ij)\,\langle\!\langle a^i_{21}(a^j_{02}+a^j_{20});a^{j'}_\alpha\rangle\!\rangle]\exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_{ij'})\\
&\qquad \simeq\frac{1}{2N}\sum_{\boldsymbol{k}}\mathcal{J}_2(\boldsymbol{k})\frac{1}{n_{01}}\chi_2(\boldsymbol{k},\omega)\\
&\qquad\quad \times\{[(1-\omega/\Delta_0)\langle a_{02}a_{02}\rangle_{\boldsymbol{k}}-(1+\omega/\Delta_0)(\langle a_{02}a_{20}\rangle_{\boldsymbol{k}}-n_0)]\\
&\qquad\quad \times[\mathcal{J}_1(\boldsymbol{q})(G_{1\alpha}(\boldsymbol{q},\omega)+G_{2\alpha}(\boldsymbol{q},\omega))-\delta_{\alpha,1}]\\
&\qquad\quad -[n_{01}-(\omega/\Delta_0)(2\langle a_{02}a_{02}\rangle_{\boldsymbol{k}}+2\langle a_{02}a_{20}\rangle_{\boldsymbol{k}}-n_{01})]\,\mathcal{J}_2(\boldsymbol{k})G_{1\alpha}(\boldsymbol{q},\omega)\}. \qquad (18)
\end{aligned}$$

Introducing these results into (5) we find that $\tilde{G}(\boldsymbol{q}, \omega)$ can be expressed in the same way as the RPA result, (6), except that (6c) is replaced by:

$$\Delta = \Delta_0 + \tfrac{1}{2}a_2 - (n_1/n_{01})(b_2(\omega) - a_2)$$

and (19)

$$\xi_{\boldsymbol{q}} = n_{01}(\mathcal{J}_1(\boldsymbol{q}) - a_1) + (n_3/n_{01})(b_1(\omega) - a_1)$$

where $n_3 \equiv n_0 + n_1 - n_{01}^2$ and

$$a_1 = \frac{n_{01}}{n_0 + n_1} \Delta \frac{1}{N} \sum_{\boldsymbol{k}} \frac{\mathcal{J}_1(\boldsymbol{k})}{D_{\boldsymbol{k}}} \eta_{\boldsymbol{k}} \tag{20}$$

and

$$b_1(\omega) = \frac{1}{N} \sum_{\boldsymbol{k}} (\mathcal{J}_1(\boldsymbol{k}))^2 \chi_1(\boldsymbol{k}, \omega). \tag{21}$$

a_2 and $b_2(\omega)$ are defined equivalently, except that $\mathcal{J}_1(\boldsymbol{k})$ is replaced by $\mathcal{J}_2(\boldsymbol{k})$ in (20) and (21). In order to obtain this expression for $\tilde{G}(\boldsymbol{q}, \omega)$ we have occasionally neglected terms of second order in a_α and $b_\alpha(\omega)$.

It is straightforward to see that the zz term, $\mathcal{J}_3(ij)$ in (1), does not contribute to the imaginary part of $\chi_1(\boldsymbol{q}, \omega)$. The quantities a_1 and a_2 are real, and only $b_1(\omega)$ and $b_2(\omega)$ give rise to a finite lifetime of the elementary excitation at $\omega = D_{\boldsymbol{q}}$. The imaginary part is

$$\operatorname{Im} \chi_1(\boldsymbol{q}, \omega) = \frac{2\Delta n_{01}(\Delta^2 - \omega^2)\Gamma(\omega)}{(D_{\boldsymbol{q}}^2 - \omega^2)^2 + [(\Delta^2 - \omega^2)\Gamma(\omega)]^2} \tag{22}$$

where

$$\begin{aligned} \Gamma(\omega) &= \frac{2\Delta n_{01}}{\Delta^2 - \omega^2} \left(\frac{n_3}{n_{01}^2} \operatorname{Im} b_1 + \frac{n_1}{n_{01}^2} \frac{\Delta^2 + \omega^2}{2\Delta^2} \operatorname{Im} b_2 \right) \\ &\cong \pi \frac{\Delta^2 - \omega^2}{2\omega} \left(\frac{n_3}{n_{01}^2} N_1(\omega) + \frac{n_1}{n_{01}^2} \frac{\Delta^2 + \omega^2}{2\Delta^2} N_2(\omega) \right). \end{aligned} \tag{23}$$

$N_1(\omega)$ and $N_2(\omega)$ are the densities of states of the x- and y-polarised excitations respectively. This result can be compared with the one deduced by Bak (1975a, b). There are higher-order differences, like $(\Delta^2 - \omega^2)\,\Gamma(\omega)$ in the denominator of (22) instead of $(\Delta^2 - D_{\boldsymbol{q}}^2)\Gamma(\omega)$, and Bak shows that the susceptibility appearing in (21) should have the self-consistently calculated value instead of the RPA result which we use in (23). There is, however, one fundamental difference between our result and that deduced by Bak. He argues that the yy coupling $(\mathcal{J}_2(ij))$ does not contribute to $\Gamma(\omega)$ in contrast to our result. In practice the difference is small as n_1 is only about 0.25–0.3 times n_3 in the temperature range of interest in Pr. If $\mathcal{J}_2(ij)$ is neglected the model is similar to the $S = \frac{1}{2}$ Ising model in a transverse field, which has been analysed thoroughly by Stinchcombe (1973).

With respect to the real parts of the corrections to Δ and $\xi_{\boldsymbol{q}}$, we first observe that the sum rule (12) is now fulfilled in the low-temperature range where n_1 and $n_3 \simeq 5n_1$ are much less than 1. It is difficult to establish precisely the area within which the decoupling procedure is valid. However, there are arguments which indicate that $\operatorname{Re}(b_\alpha(\omega) - a_\alpha)$

should be considered as spurious 'higher-order' terms in (19). If $\mathcal{J}_1(\boldsymbol{k})$ in (21) is replaced by $(1/n_{01})\,\xi_k$, then it is straightforward to show that

$$\frac{1}{N}\sum_q \mathrm{Re}[b_1(\omega = D_q) - a_1] \equiv 0$$

and equivalently for $\mathrm{Re}[b_2(\omega = D_q) - a_2]$. Hence these terms are of the order $a_\alpha \mathcal{J}_\alpha(\boldsymbol{q})/\Delta$, in which order corrections are expected, and we shall therefore neglect them. In order to be consistent we also neglect the finite-lifetime modifications due to $\mathrm{Im}\, b_\alpha(\omega)$ when performing the integration (8). In other words, the low-temperature expressions for the correlation functions and the excitation energies are taken to be valid at all temperatures. Within this presupposition the sum rule (12) is identically fulfilled at all temperatures, and the equation (11) may be safely applied.

In the limit $\beta D_q \to 0$, that is at high temperatures and/or small values of Δ_0 then $\eta_q \simeq 2/\beta D_q$. Inserting this value for η_q in (11) and (20) we get

$$a_1 \simeq \frac{1}{N}\sum_k \frac{\mathcal{J}_1(\boldsymbol{k})}{(D_k)^2}\left(\frac{1}{N}\sum_k (D_k)^{-2}\right)^{-1} \tag{24}$$

and a similar expression for a_2. With these approximate values for a_1 and a_2 our results, $\Delta = \Delta_0 + \frac{1}{2}a_2$ and $\xi_q = n_{01}(\mathcal{J}_1(\boldsymbol{q}) - a_1)$, become identical to those obtained by the correlated-effective-field method of Lines (1974, 1975).

The zz coupling, $\mathcal{J}_3(\boldsymbol{q})$, may be included in a similar way to the yy coupling. We have already mentioned that the z-polarised zero-energy excitations do not affect the lifetime of the x-polarised modes. The real contributions to $\chi_1(\boldsymbol{q}, \omega)$ appear to be of the same order of magnitude as $(n_1/n_{01})\,\mathrm{Re}(b_2(\omega) - a_2)$, and we cannot expect a valid answer unless the calculation is performed to higher order. Based on the comparison above we anticipate that the method of Lines leads to a correct estimate in this case, namely that ξ_q is unaffected whereas, to leading order in $\mathcal{J}_3(\boldsymbol{k})$,

$$\Delta = \Delta_0 + \tfrac{1}{2}a_2 - \beta n_1 \frac{1}{N}\sum_k (\mathcal{J}_3(\boldsymbol{k}))^2 \tag{25}$$

(subject to a minor adjustment of n_1 in the limit $\beta \to \infty$). These same comments apply to the zz component of the susceptibility, which should be well represented by the molecular-field model, with the one exception that it may stay finite in the zero-temperature limit, because the self-consistent RPA theory predicts a finite n_1 at $T = 0$.

3. Self-consistent RPA for praseodymium

Subject to a few modifications, the results deduced in the preceding section are applicable to the case of Pr. First, we may neglect correlation effects due to $\mathcal{J}_3(ij)$, for instance the last term of (25), because $(\mathcal{J}_3(\boldsymbol{k}))^2$ is a factor of 100 smaller than $(\mathcal{J}_1(\boldsymbol{k}))^2$. Next, we have to abandon the sharp distinction between the x and y modes. In Pr these modes are only orthogonal when $\boldsymbol{q}$ is along a b axis. As also discussed by Bak (1975a, b) the two densities of states, $N_1(\omega)$ and $N_2(\omega)$, are replaced by their average value, $N(\omega)$, so that we get $a_1 = a_2 = a$ as demanded by symmetry. Finally, the trace of the single-ion averages

$\langle a_{00}^{i} + a_{11}^{i} + a_{22}^{i}\rangle = n_0 + 2n_1$ is not equal to 1 as when $S = 1$. Instead we use

$$n_0 + 2n_1 + n_0 \sum_{p>2}^{2S+1} \exp(-\beta E_p) = 1 \tag{26}$$

where E_p are the energies relative to the ground-state of the six remaining single-ion levels. In this combined RPA–molecular-field model the internal energy per ion is

$$\begin{aligned} U &= \Delta_0(\langle a_{11}\rangle + \langle a_{22}\rangle) - 2\frac{1}{2N}\sum_q \mathcal{J}_1(\boldsymbol{q})\,(A_q^{11} + A_q^{12} + A_q^{21} + A_q^{22}) \\ &\quad + n_0 \sum_{p>2} E_p \exp(-\beta E_p) \\ &= 2\Delta_0 n_1 - (n_0 + n_1)a + n_0 \sum_{p>2} E_p \exp(-\beta E_p). \end{aligned} \tag{27}$$

The density of states, $N(\omega)$, has been calculated by Bak (1975a, b). He used the simple RPA expression for D_q, and determined the interionic couplings from the experimental dispersion in the high-symmetry directions. This procedure for determining $N(\omega)$ is subject to some uncertainties, for instance, the result depends on the value of Δ_0 used in the calculation. Bak used a value of Δ_0 of 3.2 meV, as estimated from the temperature dependence of D_q (Houmann *et al* 1975). The field dependence of the dispersion relation (Houmann *et al* 1979) indicates a slightly larger value of $\Delta_0 = 3.52$ meV. Correlation tends to increase this number by about 0.05 meV, which is less than the uncertainties involved, and we shall ignore this correction. The second moment

$$\overline{\omega^2} = \int_0^\infty \omega^2 N(\omega)\,d\omega = \frac{1}{N}\sum_q D_q^2$$

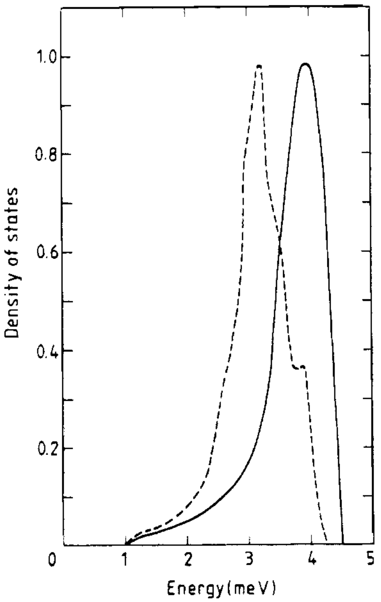

Figure 1. The density of states, $N(\omega)$, in Pr at $T = 0$. The broken line shows the result deduced by Bak (1975a, b) assuming $(\overline{\omega^2})^{1/2}$ equal to 3.20 meV. The full line shows the density of states used in the present calculations.

depends on the correlation:

$$\overline{\omega^2} = (\Delta_0 + \tfrac{1}{2}a)(\Delta_0 + \tfrac{1}{2}a + 2n_{01}a) \tag{28}$$

which implies that $N(\omega)$, at $T = 0$, has to be established in a self-consistent way. In the estimate of the correlation effects the precise form of $N(\omega)$ is not important. However, in order to isolate these contributions in a comparison with the MF (molecular-field) model, $N(\omega)$ should fulfil the relation (28). Besides this, the most important part of the spectrum is that of low frequencies, which is well characterised by the experimental results.

In figure 1 is shown $N(\omega)$ at $T = 0$ used in the present calculations. For this density of states $(\overline{\omega^2})^{1/2}$ is equal to 3.70 meV. This curve has not been determined by a microscopic model calculation, but is a plausible modification of the broken curve deduced by Bak (1975a, b) assuming $(\overline{\omega^2})^{1/2} = 3.20$ meV. The equations (11), (19), (20) and (26) were solved in a self-consistent way, and at $T = 0$ we obtained $a = 0.124$ meV and $n_1 = 0.010$. Inserted in (28) $\Delta_0 = 3.52$ meV leads to $(\overline{\omega^2})^{1/2} = 3.70$ meV consistent with $n(\omega)$ in figure 1. Adjusting $N(\omega)$ in a self-consistent manner, we solved the equations at non-zero temperatures. In figure 2 is shown the result for a as a function of T. The value of n_{01}, which is equal to 0.970 at $T = 0$, approaches the MF value very fast, and the difference is negligible above ~15 K. In figure 3 we show the temperature dependences of the excitation energies at three different values of $\boldsymbol{q}$. The MF prediction is calculated using the *total* single-ion Hamiltonian proposed by Houmann *et al* (1979). The modifications which are introduced by the self-consistent RPA calculation seems adequate in comparison with the experimental results. We note that Lindgård (1975) derived similar modifications using a simple RPA model.

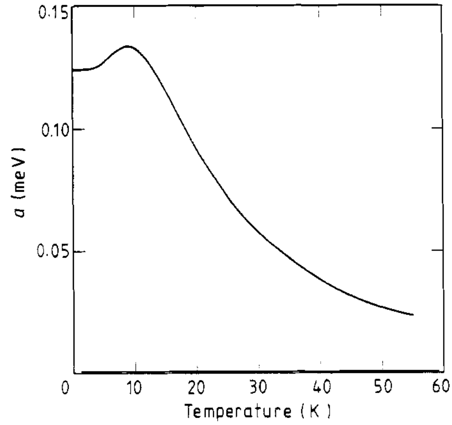

Figure 2. The correlation parameter, a, shown as a function of temperature.

At $T = 0$ the correlation between spins on different sites increases the single-spin energy, corresponding to n_1 being non-zero, but the total energy, (27), is decreased by 0.051 meV in comparison with the MF value. This energy gain is small in comparison with Δ_0. Consequently, the presence of this correlation has only minor influences on the 'effective' MF properties of the system. (The word 'effective' refers to the replacement of the bare value of $\mathcal{J}(\boldsymbol{q})$ by an appropriate effective value.) Considering the bulk

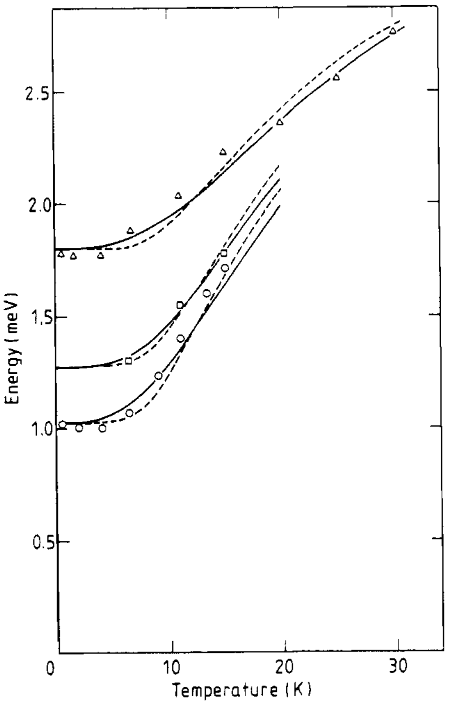

Figure 3. The excitation energies at three different q-vectors in Pr as functions of T. The lowest-lying mode on the figure is the incipient soft mode. The experimental results are from Houmann *et al* (1975). The broken lines are the MF results deduced using the model of Houmann *et al* (1979). The full lines show the results of the self-consistent RPA theory applied to the same model.

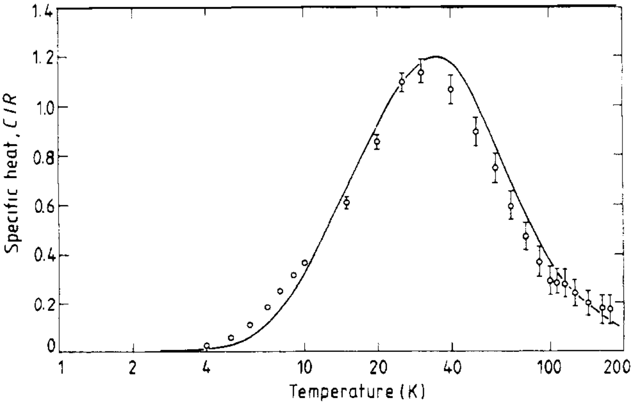

Figure 4. The magnetic specific heat of Pr as a function of temperature. The measured points are from Parkinson *et al* (1951). The full line is the RPA result using the Pr model of Houmann *et al* (1979).

susceptibility, we find that the modification introduced by the temperature variation of a is insignificant. The existing discrepancy between the high-temperature susceptibility predicted by the MF model of Houmann *et al* (1979) and the experiments remains almost unaltered. In figure 4 is shown the specific heat of Pr as a function of temperature. The theoretical result is that predicted by the model of Houmann *et al* (1979), when the correlation effects are included by (27). However, the correction to the MF result is barely visible in the figure. It is of the order of ± 0.02, and is negative in the interval 6–16 K.

4. Discussion

In § 2 we deduced the generalised susceptibility in the case of an easy-planar $S = 1$ paramagnet. The imaginary part of the self-energy is comparable with that deduced to leading order in a diagrammatic $1/Z$ expansion (Z is the number of neighbouring spins). The inclusion of the higher-order corrections remedied the failure of the simple RPA model in accounting for single-site correlation, allowing a calculation of the single-ion averages, which includes effects due to two-site correlation in a self-consistent fashion.

The self-consistent RPA model introduces a (slight) temperature dependence of the effective MF parameters, and the transition temperature is reduced in comparison with the MF model. More fundamentally, the spin fluctuations are not quenched totally at $T = 0$, and n_1 or $\Gamma(\omega)$ remains finite in this limit. The application of the model to Pr leads to a minor improvement of the theoretical temperature dependence of D_q in comparison with the experimental behaviour. In most other connections the modifications of the effective MF properties were found to be unimportant.

The density of states at $T = 0$, $N(\omega)$ in figure 1, is different from zero at quite low energies. This reflects the circumstance that Pr is close to ordering magnetically at low temperatures, and it indicates that correlation is important. On the other hand $N(\omega)$ stays small until the energy becomes close to Δ_0, because the intra-planar couplings in Pr are of very long range (see Houmann *et al* 1979). This tends to weaken the correlation.

The critical ratio is defined as

$$R = R(T) = 1 - \chi_T^0/\chi_T(\boldsymbol{Q}) \tag{29}$$

where χ_T^0 is the non-interacting susceptibility, and $\chi_T(\boldsymbol{Q}) = \chi_T(\boldsymbol{Q}, \omega = 0)$ is the static susceptibility at the wavevector $\boldsymbol{Q}$ characterising the ordered phase. By definition $R = 1$ at a second-order phase transition (at $T = T_{\mathrm{N}}$). The RPA theory leads to

$$R = 1 - (D_{\boldsymbol{Q}}/\Delta)^2 \tag{30}$$

reflecting that this theory predicts a soft-mode behaviour, $D_{\boldsymbol{Q}} \rightarrow 0$, when $T \rightarrow T_{\mathrm{N}}$. Introducing the numbers for Pr in (30) we get $R_0 = R(T \rightarrow 0) \simeq 0.918$. There exists, however, evidence that the actual R_0 is closer to 1. Between 5 and 10 K the transition induced by the application of a uniaxial stress occurs at approximately half the stress predicted by the RPA theory (K A McEwen, private communication). The RPA value of R_0 predicts the ordering, due to the nuclear spins, to occur around 45 mK, but the transition to true magnetic ordering is observed (H Bjerrum Møller and A R Mackintosh, private communication) to occur at roughly double this temperature.

Houmann *et al* (1977) and McEwen *et al* (1978, 1981) have observed a quasi-elastic peak in $\chi(\boldsymbol{q}, \omega)$ below 10 K and centred around $\boldsymbol{q} = \boldsymbol{Q}$. This peak might be due to the presence of static clusters of ordered moments surrounding local distortions in the Pr crystal (stacking faults, magnetic impurities, the surface). However, we shall now argue that most of this quasi-elastic scattering is due to a dynamic mode of slowly varying spins. The temperature dependences of the energy *and* the intensity of the incipient soft mode (see figure 3 and Bak 1975a, b) both compare with the RPA theory. Because of the Kramers–Krönig relation the integrated inelastic peak intensity then corresponds to a value of $(1-R)^{-1} \propto \chi_T(\boldsymbol{Q})$ which cannot differ very much from that determined by (30). Experimentally, $(1-R)^{-1}$ is larger by a factor of about 2 in the zero-temperature limit. This can only be consistent with the Kramers–Krönig relation if most of the extra scattering intensity around zero energy is due to a dynamic mode contributing to $\chi''(\boldsymbol{Q}, \omega)/\omega$. If we replace the non-interacting susceptibility $\chi^0(\omega)$ by $\chi^0(\omega)(1+\delta_{\omega,0}\psi)$ in the RPA expression for $\chi(\boldsymbol{q}, \omega)$, then the elastic term accounts in a phenomenological way for the elastic neutron scattering intensity, with respect to both the frequency and the $\boldsymbol{q}$ dependence. Furthermore, if we assume

$$\psi \approx 0.004\,[(\Delta/D_Q)^2 - 1]$$

then we can account reasonably well for the temperature dependence of the elastic intensity (above 3 K), the ratio between this intensity and the inelastic peak intensities, and the stress dependence of T_N. Further the extra contribution to $\chi(\boldsymbol{Q}, \omega = 0)$ implies $R_0 \simeq 0.96$, and hence $T_N \approx 100$ mK. An estimate of the contribution of the elastic term to the heat capacity (above 3 K) shows it to be of the same order of magnitude as that due to the RPA correlation. The estimate indicates that the presence of correlation plays a minor role for reducing the discrepancies in figure 4 between the calculated and the experimental values of the specific heat, also in the temperature interval between 6 and 10 K.

The appearance of the central peak in Pr below 10 K is presumably an intrinsic dynamic phenomenon due to the small value of $1 - R_0$, although the surface and impurities might influence the quantitative behaviour. We note that $1 - R(T)$ corresponds to the critical temperature parameter $\varepsilon = (T - T_N)/T$, or rather ε^γ, in a normal paramagnet. The extension of the theory in § 2, or equivalently the $1/Z$ expansion, to higher order does not, in any simple way, lead to a narrow peak at zero energy, but rather to intensities spread out in a broad band (also to regions where $N(\omega)$ is zero). The higher-order Green functions in (5) are always multiplied by $\omega \pm$ an odd integer times Δ_0 in their equations of motion, reflecting the rapid fluctuations of the spins. The central peak in the present singlet-ground-state system might be of the same origin as the central peak in systems near a structural phase transition. Ohnari (1980) has proposed that non-linear coupling between the soft mode and a thermal diffusion mode is responsible for this phenomenon.

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Note added in proof. The recent high-temperature series expansion of Johnson and Wang (1981) gives as a result that the critical ratio at $T = 0$ is $r_c = \Delta_0/2\mathcal{J}(\mathbf{0}) = 0.858$ in the case of an FCC nearest-neighbour spin-1 magnet. The present self-consistent RPA theory predicts $r_c = 0.864$, in close agreement with this result, whereas the theory of Lines gives $r_c = 0.680$. In the other limit, $\Delta_0 \rightarrow 0$, the results for T_c of the three theories coincide.

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