Generalization of the Callen and Shtrikman generating function for a Heisenberg S=1 ferromagnet to include a strong axial crystal field interaction

1990 J. Phys.: Condens. Matter 2 10451

(http://iopscience.iop.org/0953-8984/2/51/017)

J. Phys.: Condens. Matter 2 (1990) 10451–10460. Printed in the UK

Generalization of the Callen and Shtrikman generating function for a Heisenberg $S = 1$ ferromagnet to include a strong axial crystal field interaction

G J Bowden and J P D Martin
School of Physics, University of New South Wales, Kensington, NSW 2033, Australia

Received 9 April 1990

Abstract. The Callen and Shtrikman result, which demonstrates an exact correspondence between the higher order moments $\langle S_z^n \rangle$ of the Heisenberg ferromagnet calculated using either the RPA or an effective single-particle density matrix, is generalized to include a strong axial crystal field interaction. In particular, it is shown that a two parameter analogue for the Callen and Shtrikman result can be obtained for the $S = 1$ easy-axis ferromagnet, using the transformed Hamiltonian/random phase approximation (T$\mathcal{H}$/RPA).

1. Introduction

In the theory of magnetic anisotropy for localized moments, the Callen and Callen (CC) model (1966) has played a key role for many years. In this model the experimentally determined reduced-magnetization curve $M(T)/M(0)$, is used to determine a temperature dependent, single-particle effective magnetic field $x/(g\mu_B\beta)$, which reproduces the observed magnetization exactly. Once x has been determined the single-particle density matrix can be used to generate the higher moments $\langle S_z^n \rangle$ $(n \geq 2)$ required in the CC model of magnetic anisotropy. In particular, it has been shown that the agreement between magnetic anisotropy measurements and theory is often spectacular (see for example Feron *et al*, (1969), Rhyne (1972), Tajima (1971)). This observation, in itself, prompted Callen and Shtrikman (1965) to examine more closely the relationship between the $\langle S_z^n \rangle$ calculated using the simple single-particle density matrix, and those obtained using more sophisticated many-body theories such as the random phase approximation (RPA). Rather surprisingly, they were able to demonstrate that there was a one to one correspondence between the $\langle S_z^n \rangle$ moments calculated using the RPA and the single-particle model, provided the single-particle effective field $x/(g\mu_B\beta)$ is chosen so that $\langle S_Z \rangle_{sp} \equiv \langle S_Z \rangle_{RPA}$. With this result underpinning the CC model, further debate on the theory of magnetic anisotropy for localized moments practically ceased.

Nevertheless, despite the many successes of the CC model, the model only holds when the Heisenberg interaction $\mathcal{H}_{ex}$ is very much stronger than the crystal field interaction $\mathcal{H}_{CF}$. In practice, few attempts have been made to extend the CC model beyond first order perturbation theory, although Bowden (1977) has examined the consequences of taking the CC model to second order in $\mathcal{H}_{CF}$. However to our knowledge no one has been able to probe the region where $\mathcal{H}_{ex} \leq \mathcal{H}_{CF}$, despite many efforts to include crystal

0953-8984/90/5110451 + 10 \$03.50

field interactions, self-consistently, into the RPA model of the Heisenberg ferromagnet (see for example Devlin (1972), Haley and Erdös (1972), Egami and Brooks (1975), and Haley (1978)). In particular, these authors have shown that the calculated moments $\langle S_z^n \rangle$ within the RPA model cannot be obtained in a unique manner.

Recently, however, Bowden and Martin (1990) have shown that it is possible, using the T$\mathcal{H}$/RPA (transformed Hamiltonian/random phase approximation), to incorporate a strong axial crystal field interaction into the $S = 1$ Heisenberg ferromagnet, and to calculate the $\langle S_z^n \rangle$ uniquely. In this paper, the T$\mathcal{H}$/RPA is used to generate a two parameter analogue of the Callen and Shtrikman result for the $S = 1$ ferromagnet, given that the preferred direction of magnetization is collinear with the axially symmetric crystal field interaction.

2. $S = 1$ ferromagnet with a strong axially symmetric crystal field interaction

A Heisenberg ferromagnet with an axially symmetric quadratic crystal field can be written in the form

$$\mathcal{H} = -\sum_i g\mu_B B_{\text{app}} S_Z(i) - \frac{1}{2}\sum_{\{ij\}} \{J_{ij}\boldsymbol{S}(i)\cdot\boldsymbol{S}(j) + K_{ij}S_Z(i)S_Z(j)\}$$
$$- \sum_i \frac{D}{\sqrt{6}}\{3S_Z(i)^2 - S(S+1)\} \qquad (1)$$

where J_{ij} (K_{ij}) is the isotropic (anisotropic) exchange between the ith and jth atoms, D is the axially symmetric second order crystal field parameter, and the remaining terms possess their usual meaning. In this paper, only the case of $D > 0$ will be considered. Thus the easy direction of the magnetization lies along the z axis. Note that higher rank crystal field interactions can have no effect on the $S = 1$ spin ensemble.

From Bowden and Martin (1990), it can be shown that the T$\mathcal{H}$/RPA model yields the following unique solutions, for the $S = 1$ easy axis ferromagnet:

$$\langle \hat{T}_0^1 \rangle = (1/\sqrt{2})\langle S_z \rangle = (1 + 2\varphi_1)/[\sqrt{2}(1 + 3\varphi_1 + 3\varphi_1^2 + \varphi_2 - 3\varphi_2^2)] \qquad (2)$$

and

$$\langle \hat{T}_0^2 \rangle = (1/\sqrt{6})(3\langle S_z^2 \rangle - 2) = (1 - 2\varphi_2)/[\sqrt{6}(1 + 3\varphi_1 + 3\varphi_1^2 + \varphi_2 - 3\varphi_2^2)] \qquad (3)$$

where

(i) the thermal weighting factors are given by

$$\varphi_1 = \frac{1}{N}\sum_k \frac{1}{2}\left(\frac{1}{[\exp(\beta E_1(k)) - 1]} + \frac{1}{[\exp(\beta E_2(k)) - 1]}\right) \qquad (4)$$

$$\varphi_2 = \frac{1}{N}\sum_k \frac{1}{2}\left(\frac{1}{[\exp(\beta E_1(k)) - 1]} - \frac{1}{[\exp(\beta E_2(k)) - 1]}\right) \qquad (5)$$

(ii) the two excitation branches $E_1(k)$ and $E_2(k)$ appearing in equations (4) and (5) are given by

$$E_1(k) = g\mu_B B_{app} + \sqrt{2}\langle \hat{T}_0^1\rangle(J(0) + K(0) - \tfrac{1}{2}J(k)) + (\sqrt{3}/\sqrt{2})(D - \langle \hat{T}_0^2\rangle J(k)) \tag{6}$$

$$E_2(k) = g\mu_B B_{app} + \sqrt{2}\langle \hat{T}_0^1\rangle(J(0) + K(0) - \tfrac{1}{2}J(k)) - (\sqrt{3}/\sqrt{2})(D - \langle \hat{T}_0^2\rangle J(k)) \tag{7}$$

(iii)

$$J(k) = \sum_j J_{ij} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{\delta}_{ij}) \tag{8}$$

(iv) $\boldsymbol{\delta}_{ij}$ are the nearest neighbour vectors. Note that in arriving at equations (2) and (3) irreducible tensor operators $\hat{T}_q^n$ have been employed rather than their Cartesian counterparts S_z and $S_\pm$, because of the former's superior commutation, construction, contraction and rotational properties (e.g. Buckmaster *et al* (1972)).

In practice, equations (2)–(8) can be used to calculate the ensemble averages $\langle \hat{T}_0^1\rangle$ and $\langle \hat{T}_0^2\rangle$ at any temperature, self-consistently.

3. Extension of the Callen and Callen result

Many authors have shown (see for example Tahir-Kheli and ter Haar 1962) that when the crystal field parameter $D = 0$, the magnetization for an $S = 1$ ferromagnet, in the random phase approximation can be expressed in the form

$$\langle \hat{T}_0^1\rangle = (1/\sqrt{2})\langle S_z\rangle = (1 + 2\varphi)/[\sqrt{2}(1 + 3\varphi + 3\varphi^2)]. \tag{9}$$

The single thermal weighting function φ in equation (9) is of the form

$$\varphi = \frac{1}{N}\sum_k \left(\frac{1}{[\exp(\beta E(k)) - 1]}\right) \tag{10}$$

with a single excitation branch

$$E(k) = g\mu_B B_{app} + \sqrt{2}\langle \hat{T}_0^1\rangle(J(0) + K(0) - J(k)) \tag{11}$$

which is the usual spin-wave result.

In order to make contact with the single-particle effective field model, Callen and Shtrikman define an effective field parameter x such that

$$\varphi \equiv 1/(\mathrm{e}^x - 1). \tag{12}$$

Further, on substituting equation (12) into (9) they observed that

$$\langle \hat{T}_0^1\rangle = (1/\sqrt{2})\langle S_z\rangle = (1/\sqrt{2})(\mathrm{e}^x - \mathrm{e}^{-x})/(\mathrm{e}^x + 1 - \mathrm{e}^{-x}) \tag{13}$$

which is identical to the result obtained using the single-particle density matrix

$$\rho = \mathrm{e}^{xS_z}/\mathrm{Tr}[\mathrm{e}^{xS_z}]. \tag{14}$$

Thus the parameter $x/(g\mu_B\beta)$ can be viewed as a temperature renormalized effective field acting on a single spin. In addition, Callen and Shtrikman (1965) demonstrated that the higher order moments $\langle S_z^n\rangle$ obtained from the single-particle model defined by equations (12)–(14), were identical to the moments calculated using the RPA, for all S.

In essence, this procedure works because there is a one to one correspondence between the single degenerate branch $E(k)$ in the RPA, and its single ion counterpart

$$E_{|S_z+1\rangle} - E_{|S_z\rangle} = E_{|S_z\rangle} - E_{|S_z-1\rangle} = x/kT. \tag{15}$$

In the T$\mathcal{H}$/RPA model however, there are two weighting factors φ_1 and φ_2 for the $S = 1$ ferromagnet, in place of the single factor φ discussed above. In the presence of the crystal field interaction therefore, it is necessary to define a new single-particle density matrix which includes both magnetic and quadrupole parameters. In place of equation (14) therefore we write

$$\rho = [\![\exp\{xS_Z + (y/\sqrt{6})[3S_Z^2 - S(S+1)]\}]\!]/\mathrm{Tr}[\![\exp\{xS_Z + (y/\sqrt{6})[3S_Z^2 - S(S+1)]\}]\!] \tag{16}$$

For $S = 1$, this single-particle model has two $\Delta m = \pm 1$ transitions

$$E_{|1\rangle} - E_{|0\rangle} = [x + (3y/\sqrt{6})]k_{\mathrm{B}}T \tag{17}$$

$$E_{|0\rangle} - E_{|-1\rangle} = [x - (3y/\sqrt{6})]k_{\mathrm{B}}T \tag{18}$$

which are the single-particle counterparts of $E_1(k)$ and $E_2(k)$.

Next, we define x and y via the combinations

$$\varphi_1 + \varphi_2 = \frac{1}{N}\sum_k \left(\frac{1}{[\exp(\beta E_1(k)) - 1]}\right) \equiv \frac{1}{\{\exp[x + (3y/\sqrt{6})] - 1\}} \tag{19}$$

$$\varphi_1 - \varphi_2 = \frac{1}{N}\sum_k \left(\frac{1}{[\exp(\beta E_2(k)) - 1]}\right) \equiv \frac{1}{\{\exp[x - (3y/\sqrt{6}) - 1\}} \tag{20}$$

This ensures that both the many body and single-particle descriptions possess the same occupation number. Secondly, on substituting (19) and (20) into the many body expressions for $\langle T_0^1\rangle$ and $\langle T_0^2\rangle$ it is easily shown that

$$\langle \hat{T}_0^1\rangle = \frac{1}{\sqrt{2}}\langle S_Z\rangle = \frac{\exp[x + (y/\sqrt{6})] - \exp[-x + (y/\sqrt{6})]}{\sqrt{2}\{\exp[x + (y/\sqrt{6})] + \exp[-(2y/\sqrt{6})] + \exp[-x + (y/\sqrt{6})]\}} \tag{21}$$

$$\langle \hat{T}_0^2\rangle = \frac{1}{\sqrt{6}}\{3\langle S_z^2\rangle - 2\} = \frac{\exp[x + (y/\sqrt{6})] - 2\exp[-(2y/\sqrt{6})] + \exp[-x + (y/\sqrt{6})]}{\sqrt{6}\{\exp[x + (y/\sqrt{6})] + \exp[-(2y/\sqrt{6})] + \exp[-x + (y/\sqrt{6})]\}} \tag{22}$$

which are identical to the single-particle averages obtained using equation (16). Further, using the identity that $\langle \hat{T}_0^n\rangle = 0$ for $S = 1$ when $n > 2$, it is easily shown that $\langle S_z\rangle = \langle S_z^3\rangle = \langle S_z^5\rangle$ etc., and $\langle S_z^2\rangle = \langle S_z^4\rangle$ etc., for both the T$\mathcal{H}$/RPA and its single-particle equivalent. Thus the temperature renormalized effective single-particle density matrix of equation (16), yields the same ensemble averages as the many body T$\mathcal{H}$/RPA.

4. Free energy considerations

In the presence of a small additional magnetic field $\boldsymbol{B}'$, the Hamiltonian for the spin system in question can be written in the form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \tag{23}$$

where (i) $\mathcal{H}_0$ is given by equation (1), (ii)

$$\mathcal{H}' = \sum_i g\mu_B \boldsymbol{J}_i \cdot \boldsymbol{B}' = g_B \mu B' \sum_i [J_Z(i)\cos(\theta) + J_X(i)\sin(\theta)] \tag{24}$$

and (iii) θ is the angle between $\boldsymbol{B}'$ and the z axis. Note that we have constrained $\boldsymbol{B}'$ to lie in the zx plane. Consequently, we may make use of perturbation theory (e.g. Bowden (1977)) to show that the free energy can be written in the form

$$F = F_0 + F_1 + F_2 + \ldots \tag{25}$$

where F_0 is the unperturbed free energy,

$$F_1 = \langle \mathcal{H}' \rangle = -\boldsymbol{M} \cdot \boldsymbol{B}' \tag{26}$$

$$F_2 = \tfrac{1}{2}\beta\left[\left\langle \mathcal{H}' \int \mathcal{H}' \right\rangle - \langle \mathcal{H}' \rangle^2\right] = \frac{1}{2}\beta[\boldsymbol{B}' \cdot \boldsymbol{\chi} \cdot \boldsymbol{B}'] \tag{27}$$

In equation (27), $\boldsymbol{\chi}$ is the magnetic susceptibility tensor. More details of the ensemble average $\langle A \int B \rangle$ can be found in the paper by Bowden (1977).

If we now employ the equivalence between the T$\mathcal{H}$/RPA, and the equivalent single-particle model of equation (16), we find

$$F_1 = N(g\mu_B B')\langle S_Z \rangle \cos(\theta) \tag{28}$$

$$F_2 = -\frac{1}{2}\beta N(g\mu_B B')^2\left[(\langle S_Z^2 \rangle - \langle S_Z \rangle^2)\cos^2(\theta) + \left(\left\langle S_X \int S_X \right\rangle\right)\sin^2(\theta)\right]$$

$$= -\frac{1}{2}\beta N(g\mu_B B')^2\left[(\langle S_Z^2 \rangle - \langle S_Z \rangle^2)\cos^2(\theta)\right.$$

$$\left. + \frac{1}{2}\left(\frac{3\langle S_Z^2 \rangle + \langle S_Z \rangle - 2}{[x + (3y/\sqrt{6})]} - \frac{3\langle S_Z^2 \rangle - \langle S_Z \rangle - 2}{[(x - (3y/\sqrt{6})]}\right)\sin^2(\theta)\right] \tag{29}$$

These expressions can be used to compute the principal susceptibility components χ_{xx} and χ_{zz}, and the torque $\boldsymbol{\Gamma} = \boldsymbol{M} \times \boldsymbol{B}'$ ($= \partial F/\partial\theta$) experienced by the ferromagnet in a

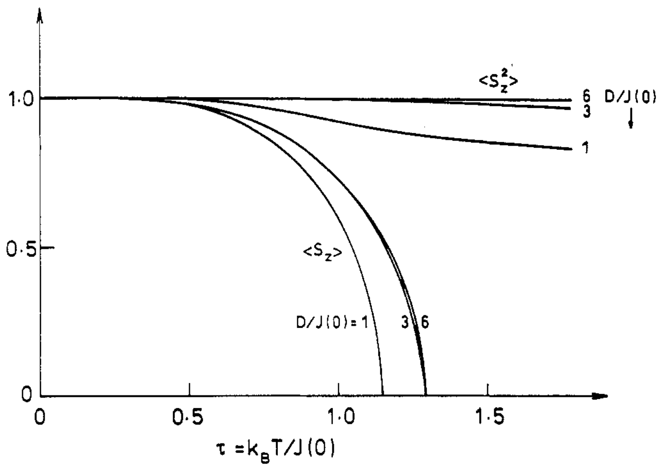

Figure 1. Calculated values of $\langle S_Z \rangle$ and $\langle S_Z^2 \rangle$ versus temperature for various values of $D/J(0)$.

weak applied magnetic field $\boldsymbol{B}'$. Whilst the result for χ_{zz} $[\alpha(\langle S_Z^2 \rangle - \langle S_Z \rangle^2)]$ is exact, the expression for χ_{xx} (the last term in equation (29)), is based on the assumption that

$$\left\langle S_X \int S_X \right\rangle_{\mathrm{T}\mathscr{H}/\mathrm{RPA}} = \left\langle S_X \int S_X \right\rangle_{\mathrm{sp}}. \tag{30}$$

In practice, it is difficult to obtain an expression for $\langle S_X \int S_X \rangle$ within the RPA model. However due to the equivalence between the T$\mathscr{H}$/RPA and the single particle model, we believe that equation (30) is likely to be a good approximation. In passing we note that both $\langle S_X \int S_X \rangle_{\mathrm{T}\mathscr{H}/\mathrm{RPA}}$ and $\langle S_X \int S_X \rangle_{\mathrm{sp}}$ possess the same upper bound $[S(S+1) - \langle S_Z^2 \rangle]/2$, and lower bound 0.

To illustrate the above results, we have calculated the ensemble averages $\langle S_Z \rangle$ and $\langle S_Z^2 \rangle$, χ_{zz} and χ_{xx} for the cases of $D/J(0) = 1, 3, 6$ (when $K(0) = 0$). The results can be seen in figures 1 and 2 respectively. Note that these results have been calculated for the special case of a face centred cubic lattice. Given $\langle S_Z \rangle$ and $\langle S_Z^2 \rangle$ it is also possible to extract the equivalent single particle model parameters $x/(g\mu_B\beta)$ and $y/(g\mu_B\beta)$, which are shown in figure 3. It will be observed that $x/(g\mu_B\beta)$ decreases as $T \to 0$ K. This feature is also present in the ordinary RPA model of Tahir Kheli and ter Haar (1962). In the ordinary RPA it can be shown that as $T \to 0$ K, $x/(g\mu_B\beta) \to 0$ while $x \to \infty$. However in the T$\mathscr{H}$/RPA model

$$\lim_{T\to 0}[x/(g\mu_B\beta)] \to \sqrt{2}\langle \hat{T}_0^1 \rangle (K(0) + J(0)/2) \tag{31}$$

$$\lim_{T\to 0}[y/(g\mu_B\beta)] \to D - \langle \hat{T}_0^1 \rangle J(0)/\sqrt{3}. \tag{32}$$

Note that as D is increased, the effective quadrupole parameter $y/(g\mu_B\beta)$ remains fairly constant over the whole temperature range, in accord with equation (32). More details of the behaviour of $\langle S_Z \rangle$ and $\langle S_Z^2 \rangle$ etc., in the limit $T \to 0$ K are given in the appendix,

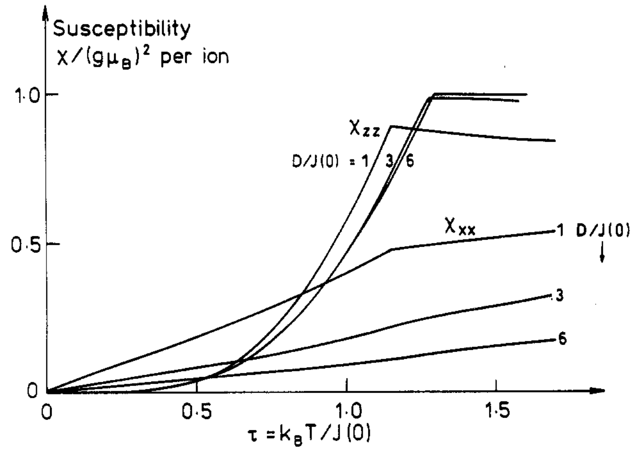

Figure 2. Longitudinal and transverse susceptibility components χ_{zz} and χ_{xx} for various values of $D/J(0)$.

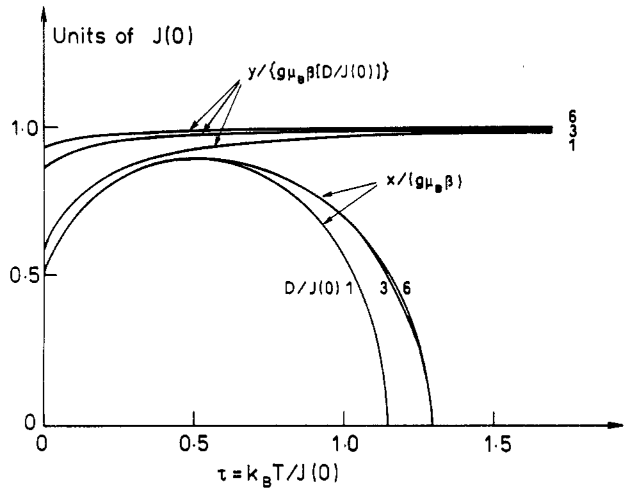

Figure 3. Calculated values of the effective single particle parameters $x/(g\mu_B\beta)$ and $y(g\mu_B\beta)$ obtained from the results shown in figure 1.

where similar expressions to the low temperature expansion of Tahir Kheli and ter Haar (1962), are presented and discussed.

5. Conclusions

We have shown how the Callen and Shtrikman result can be generalized to the case of an $S = 1$ ferromagnet subject to a strong uniaxial crystal field interaction. In place of a single parameter x, two parameters x and y are now required. However once x and y have been determined, there is a one to one correspondence between the moments $\langle S_Z^n \rangle$ of both the T𝒦/RPA and the single-particle model. These results have subsequently been used to derive explicit expressions for the free energy of the ferromagnet in the presence of a small additional magnetic field $\boldsymbol{B}'$. Whilst the results given for F_1 and χ_{zz} are exact (within the T$\mathcal{K}$/RPA), in practice it was necessary to make an additional assumption in order to obtain an expression for χ_{xx}. In summary therefore, equations (28) and (29) can be viewed as the strong crystal field counterpart of the CC model. They could be used, for example, to compute the torque $\boldsymbol{\Gamma} = \boldsymbol{M} \times \boldsymbol{B}'$ $(= \partial F/\partial \theta)$ experienced by the ferromagnet in a weak applied magnetic field. Finally, we stress that the expressions obtained in this paper apply to $S = 1$ spin systems only. In a following paper however, we will demonstrate that the two parameter analogue of the Callen and Shtrikman result, also holds for $S = 3/2$ spin ensembles.

Appendix. Thermal weighting factors at low temperature

Starting from the thermal weighting function φ defined by equations (10) and (11), with both B_{app} and $K(0)$ set equal to zero, Tahir Kheli and ter Haar (1962) obtain the following low temperature expansion

$$\lim_{T\to 0} \varphi = \lim_{T\to 0}\left\{\frac{1}{N}\sum_k \left[\exp\left(\frac{\hbar\langle S_Z\rangle[J(0) - J(k)]}{k_B T}\right) - 1\right]^{-1}\right\} \tag{A1}$$

$$= \left(\frac{6k_B T}{4\pi\nu\hbar J(0)\langle S_Z\rangle}\right)^{3/2} \zeta(\tfrac{3}{2}) + a_1\left(\frac{6k_B T}{4\pi\nu\hbar J(0)\langle S_Z\rangle}\right)^{5/2} \zeta(\tfrac{5}{2}) + a_2\left(\frac{6k_B T}{4\pi\nu\hbar J(0)\langle S_Z\rangle}\right)^{7/2} \zeta(\tfrac{7}{2}) + \ldots \tag{A2}$$

where

$$\text{(i) } a_1 = \tfrac{3}{4}\pi\nu \qquad a_2 = \pi^2\omega\nu^2 \tag{A3}$$

$$\text{(ii) } \zeta(n) = \sum_{r=1}^{\infty} r^{-n} \qquad \text{(the Riemann zeta function)} \tag{A4}$$

$$\begin{aligned} &\text{(iii) } \nu = 1 && \omega = 33/32 && (\text{SC}) \\ &\nu = \tfrac{3}{4}2^{2/3} && \omega = 281/288 && (\text{BCC}) \\ &\nu = 2^{1/3} && \omega = 15/16 && (\text{FCC}). \end{aligned} \tag{A5}$$

Thus at low temperatures $\langle S_Z\rangle$ falls as $T^{3/2}$, in accord with the spin wave result. Note that our definition of $J(0)$ in equation (A1) and (A2) is twice the value used by Tahir Kheli and ter Haar (1962).

In the case of the T$\mathcal{K}$/RPA, it is also possible to obtain analogous expressions to that of equation (A2). In practice, it is convenient to examine the low temperature expansions of the combinations $\varphi_1 \pm \varphi_2$, because these combinations involve $E_1(k)$ and $E_2(k)$ separately (see equations (19) and (20)). Once low temperature expressions for $\varphi_1 \pm \varphi_2$

have been derived, it is a relatively easy matter to determine φ_1 and φ_2, and hence $\langle \hat{T}_0^1 \rangle$ ($\langle S_Z \rangle/\sqrt{2}$) and $\langle \hat{T}_0^2 \rangle$ using equations (2) and (3), respectively. For $\varphi_1 + \varphi_2$ we find

$$\begin{aligned}\lim_{T\to 0}[\varphi_1 + \varphi_2] &= \lim_{T\to 0}\left\{\frac{1}{N}\sum_k \left[\exp\left(\frac{E_1(k)}{k_B T}\right) - 1\right]^{-1}\right\} \\ &= \left(\frac{6k_B T}{4\pi\nu\hbar J(0)[\langle \hat{T}_0^1\rangle + \sqrt{3}\langle \hat{T}_0^2\rangle]/\sqrt{2}}\right)^{3/2} Z_{3/2}\left[\frac{A}{k_B T}\right] \\ &\quad + a_1\left(\frac{6k_B T}{4\pi\nu\hbar J(0)[\langle \hat{T}_0^1\rangle + \sqrt{3}\langle \hat{T}_0^2\rangle]/\sqrt{2}}\right)^{5/2} Z_{5/2}\left[\frac{A}{k_B T}\right] \\ &\quad + a_2\left(\frac{6k_B T}{4\pi\nu\hbar J(0)[\langle \hat{T}_0^1\rangle + \sqrt{3}\langle \hat{T}_0^2\rangle]/\sqrt{2}}\right)^{7/2} Z_{7/2}\left[\frac{A}{k_B T}\right] + \dots \end{aligned} \qquad \text{(A6)}$$

where

(i) $E_1(k)$ is given by equation (4)

(ii) $Z_n\left[\frac{A}{k_B T}\right] = \sum_{r=1}^{\infty} r^{-n} \exp\left[\frac{-rA}{k_B T}\right]$ (A7)

(iii) $A = \sqrt{2}\langle \hat{T}_0^1\rangle K(0) + (\langle \hat{T}_0^1\rangle - \sqrt{3}\langle \hat{T}_0^2\rangle)/\sqrt{2} + (\sqrt{3}/\sqrt{2})D$ (A8)

(iv) a_1 and a_2 are given in equation (A3)

(v) ν and ω are given in equation (A5).

Note that at $T = 0$ K $\langle \hat{T}_0^1\rangle = \sqrt{3}\langle \hat{T}_0^2\rangle$ ($= S/\sqrt{2}$), which leads to simplified expressions for (A6) and (A8).

For $\varphi_1 - \varphi_2$ we obtain

$$\begin{aligned}\lim_{T\to 0}[\varphi_1 - \varphi_2] &= \lim_{T\to 0}\frac{1}{N}\sum_k \left\{\left[\exp\left(\frac{E_2(k)}{k_B T}\right) - 1\right]^{-1}\right\} \\ &= [\![\exp\{(\hbar/k_B T)[(-\sqrt{3}/\sqrt{2})D + \sqrt{2}\langle \hat{T}_0^1\rangle(J(0) + K(0))]\} - 1]\!]^{-1}. \end{aligned} \qquad \text{(A9)}$$

Thus equations (A6) and (A9) can be used to calculate φ_1 and φ_2, and hence obtain low temperature expansions for $\langle S_Z\rangle$ and $\langle S_Z^2\rangle$.

In order to compare our results with the well known low temperature expansions of $\langle S_Z\rangle$ given by Dyson (1956) and Tahir Kheli and ter Haar (1962), we set D, B_{app} and $K(0)$ all equal to zero. We find

$$\begin{aligned}\langle S_Z\rangle_{\substack{S=1\\D=0}} &= S - (6k_B T/4\pi\nu\hbar J(0)S)^{3/2}\zeta(\tfrac{3}{2}) \\ &\quad + (6k_B/4\pi\nu\hbar J(0)S)^3(T^2\hbar J(0)/2k_B)\zeta(\tfrac{3}{2})\zeta(\tfrac{1}{2}) + \dots. \end{aligned} \qquad \text{(A10)}$$

Thus the T𝒳/RPA predicts that $\langle S_Z\rangle$ will decrease as $T^{3/2}$ when $D = 0$, even though the model only strictly holds for large crystal field parameters.

References

Bowden G J 1977 *J. Phys. F: Met. Phys.* **7** 1731–46
Bowden G J and Martin J P D 1990 *J. Phys.: Condens. Matter.* **2** 10435–50
Bowden G J, Martin J P D and Oitmaa J 1986 *J. Phys. C: Solid State Phys.* **19** 551–61
Buckmaster H A, Chatterjee R and Shing Y H 1972 *Phys. Status Solidi* **13** 9–50

Callen H B and Callen E 1966 *J. Phys. Chem. Solids* **27** 1271–85
Callen H B and Shtrikman S 1965 *Solid State Commun.* **3** 5–9
Devlin J F 1972 *Phys. Rev.* B **4** 136–46
Dyson F J 1956 *Phys. Rev.* **102** 1230–44
Egami T and Brooks M S S 1975 *Phys. Rev.* B **12** 1021–8, 1029–37
Feron J L, Gerard H and Pauthenet R 1969 *Les Elements des Terres Rares* (Paris: CNRS) p 19–30
Haley S B and Erdös P 1972 *Phys. Rev.* B **5** 1106–19
Haley S B 1978 *Phys. Rev.* B **17** 337–46
Rhyne J J 1972 *Magnetic Properties of Rare Earth Metals* ed R J Elliott (London: Plenum)
Tajima K 1971 *J. Phys. Soc. Japan* **31** 441–51
Tahir Kheli R and ter Haar D 1962 *Phys. Rev.* **127** 88–94