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Abstract. This paper presents a discussion about a spin model arising out of single- and double-electron exchange processes. The Hamiltonian which consists of the usual Heisenberg exchange, biquadratic exchange and three-atom coupling is studied using the Green function equation-of-motion method within the random-phase approximation. The effects of biquadratic exchange and three-atom coupling on the magnetization curves, quadrupolar ordering and the transition temperature T_C are studied. It is shown that the magnetization changes from second to first order at T_C depending on the strengths of the biquadratic and three-atom coupling. It is also seen that T_C becomes equal to zero at certain values of the parameters. The results are compared with those of molecular-field theory.

1. Introduction

It was shown by Munro and Girardeau (1976) that, when there are two electrons present in an unfilled shell, both single-electron exchange and double-electron exchange processes occur, resulting in a biquadratic exchange term and a three-atom coupling term in addition to the usual Heisenberg bilinear exchange. This kind of spin model is usually believed to arise from complicated spin arrangements, such as canted or spiral spin configurations, or from the simple antiferromagnetic case. However, we shall restrict this discussion to ferromagnets only. Considering nearest-neighbour interactions, one can describe the above exchange processes by means of the following Hamiltonian:

$$H = -\omega_0 \sum_i S_i^z - \sum_{\langle ij \rangle} J_{ij}(S_i \cdot S_j) - \sum_{\langle ij \rangle} J'_{ij}(S_i \cdot S_j)^2 - \sum_{\langle ijl \rangle} L_{ijl}(S_i \cdot S_j)(S_j \cdot S_l) \qquad (1)$$

where $\omega_0 = \mu H_a$, μ is the magnetic moment per atom, H_a is the applied magnetic field, J_{ij} is the usual bilinear Heisenberg exchange integral arising from the single-electron exchange, and J'_{ij} and L_{ijl} are the biquadratic and three-atom exchange interactions respectively, arising from the double-electron exchange process.

The above Hamiltonian for the special case $L_{ijl} = 0$ has been studied extensively in the past (Adler et al 1976, Chakraborty 1976, 1977, 1989, Tiwari and Srivastava 1980) and the case with $J'_{ij} = 0$ was studied by Akasmit and Westwansky (1978), Adler and Oitmaa (1979) and Mitra and Chakraborty (1994, hereafter referred to as I).

The complete Hamiltonian expressed by equation (1) has not yet been studied. Only a restricted case was considered by Munro and Girardeau (1976) using the molecular-field

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approximation (MFA). They considered that $L_{ijl} = \lambda' J'_{ij}$ so that L_{ijl} vanishes simultaneously with J'_{ij} (λ' being a parameter).

The purpose of the present paper is to study equation (1) without any of the restrictions mentioned above. We shall use the method of double-time thermal Green functions and utilize the random-phase approximation for decoupling the higher-order Green functions. The method is the same as used by us in I. The chief motivation is to study the competition between the biquadratic exchange and the three-atom exchange. The plan of the paper is as follows.

Section 2 presents the necessary mathematical equations for deriving the energy spectrum and other thermodynamic quantities. Section 3 contains some suitable approximations for computing the statistical variables. The results and discussion are presented in section 4. Section 5 contains some concluding remarks.

2. Green functions and energy spectrum

The Green function equation-of-motion method using the random-phase approximation was developed in I by the present authors for a Heisenberg ferromagnet with three-atom exchange, i.e. for the case with $J_{ij} \neq 0$, $L_{ijl} \neq 0$, $J'_{ij} = 0$. To include the biquadratic exchange we proceed along the same lines as the method in I. We consider the following Fourier-transformed Green functions:

$$G_1 = \langle\langle S_k^+; S_q^- \rangle\rangle \tag{2a}$$

$$G_2 = \langle\langle \sigma_k^+; S_q^- \rangle\rangle \tag{2b}$$

where k and q are the momentum indices and

$$\sigma_k = S_k^z S_k^+ + S_k^+ S_k^z. \tag{3}$$

The equations of motion can be shown to be

$$(\omega - \omega_0 - A_k)G_1 - C_k G_2 = \frac{\langle S_{k-q}^z \rangle}{\pi N^{1/2}} \tag{4a}$$

$$(\omega - \omega_0 - B_k)G_2 + D_k G_1 = \frac{\langle \lambda_{k-q} \rangle}{\pi N^{1/2}} \tag{4b}$$

where

$$A_k = 2m(J_0 - J_k) - \tfrac{2}{3}(4 - \lambda)mL_{kk} + \tfrac{2}{3}(2 + \lambda)mL_{00} - \lambda m L_{0k} \tag{5}$$

$$B_k = 2J_0(1 - \tfrac{3}{2}\alpha')m - \alpha' m J_k - \lambda m L_{0k} + \tfrac{4}{3}mL_{00} + \tfrac{2}{3}\lambda m L_{00} \tag{6}$$

$$C_k = m^2(L_{00} - L_{0k}) + \alpha'\lambda(J_0 - J_k) \tag{7}$$

$$D_k = \tfrac{1}{3}\lambda L_{kk}(4 - \lambda) - m^2(L_{00} - L_{0k}) - \tfrac{8}{3}\alpha' J_0 + 2(1 - \tfrac{1}{2}\alpha')\lambda J_k - \tfrac{1}{3}\alpha'\lambda J_0 \tag{8}$$

with $m = \langle S^z \rangle$ being the spontaneous magnetization and $\lambda = 3\langle (S^z)^2 \rangle - 2$ the quadrupolar ordering parameter. J_k, L_{kk}, L_{0k} and L_{00} are the Fourier-transformed interaction constants. The parameters α' are defined as $\alpha' = J'/J$, with J, J' being the nearest-neighbour bilinear

and biquadratic exchange constants, respectively. Equations (4a) and (4b) resulted from the random-phase approximation used to decouple the higher-order Green functions appearing in the corresponding equations of motion. Solving these two equations, we finally arrive at the following expression for the energy spectrum:

$$\omega_k = \omega_0 + 2m(J_0 - J_k) - M'_k \pm \sqrt{M_k} \tag{9}$$

where

$$M'_k = 2\alpha' m J_0 + \tfrac{1}{3}m(4 - \lambda)L_{kk} + 2\lambda m L_{00} - \tfrac{4}{3}m(2 + \lambda)L_{00}$$

$$
\begin{aligned}
M_k = {} & [mJ_k(1 - \alpha') - \alpha' m J_0 + \tfrac{1}{6}m(4 - \lambda)L_{kk} - m^2(L_{00} - L_{0k})]^2 \\
& - m^2(L_{00} - L_{0k})[2J_k(\lambda - m) + \tfrac{1}{3}(4 - \lambda)(\lambda - m)L_{kk} \\
& + 2\alpha' m(J_0 + J_k) - \tfrac{4}{3}\alpha'(\lambda + 2)J_0] \\
& - \alpha'\lambda(J_0 - J_k)[\tfrac{1}{3}\lambda(4 - \lambda)L_{kk} - \tfrac{1}{3}\alpha' J_0(\lambda + 8) + \lambda J_k(2 - \alpha')].
\end{aligned}
\tag{10}
$$

Equation (9) gives us two branches of energy spectra. However, both these spectra are not physically acceptable. The physical validity is tested by inspection of the ground-state form. Two such limiting cases are well known: one for $\alpha = 0$ and the other for $\alpha' = 0$. In the first case, the energy spectrum remains unaffected, for the spin-1 model, at $T = 0$ and in the second case the exact form has been determined and is given in the literature. These two cases are satisfied if we consider only the negative sign in equation (9). Henceforth we shall therefore consider only the negative sign.

3. Approximate forms for physical quantities

Although we shall concentrate only a single energy branch, it is very difficult to carry out further simplifications for the derivation of different physical quantities unless some appropriate approximations are made. Firstly, we use the nearest-neighbour approximations for L so that

$$
\begin{aligned}
L_{00} &= z(z - 1)\alpha J \\
L_{0k} &= z(z - 1)\alpha J \gamma_k \\
L_{kk} &= z(z\gamma_k^2 - 1)\alpha J
\end{aligned}
\tag{11}
$$

with $\gamma_k = (1/z)\sum_k \exp(ik \cdot \delta)$, δ being the nearest-neighbour vector and z being the number of nearest neighbours. $\alpha = L/J$, where L is the nearest-neighbour three-atom coupling constant. The energy spectrum thus reduces to the following form:

$$\omega_k = \omega_0 + 2mJz(1 - \gamma_k)[1 - \tfrac{1}{2}\alpha' + a\alpha z + b\alpha + a\alpha z\gamma_k + f(\gamma_k)] \tag{12}$$

where

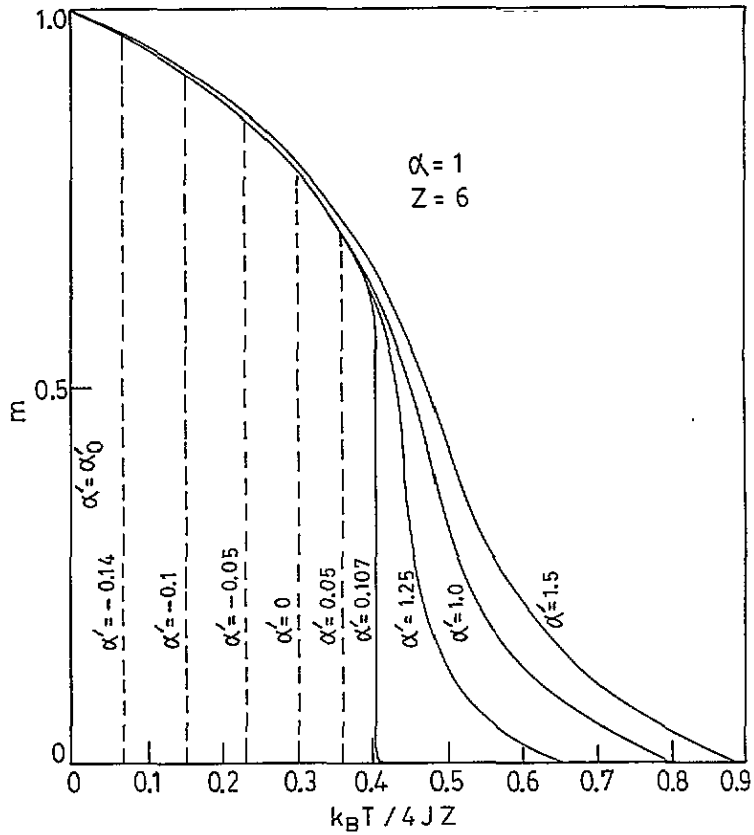$$f(\gamma_k) = \frac{A - B\gamma_k - C\gamma_k^2}{D - E\gamma_k - N\gamma_k^2}$$

Figure 1. Magnetization curves for a Heisenberg ferromagnet with biquadratic and three-atom interactions: m is plotted against $k_B T/4Jz$ for $\alpha = 1$, $z = 6$. The ordinate is shown by a thick line which corresponds to $\alpha' = \alpha_0$. The broken lines refer to the first-order transition. The curves for $\alpha' \geqslant 0.107$ correspond to second-order transitions.

with

$$A = u[a\alpha(\lambda - m) - \alpha'm + \tfrac{2}{3}\alpha'(\lambda + 2)] + \tfrac{1}{2}\alpha'[a\alpha + \tfrac{1}{6}\alpha'(8 + \lambda)]$$

$$B = u(\lambda - m + \alpha'm) + \tfrac{1}{4}\alpha'^2(2 - \alpha')$$

$$C = N[u(\lambda - m) + \tfrac{1}{2}\alpha'\lambda]$$

$$D = a\alpha + \alpha' + 2um$$

$$E = 1 - \alpha' + 2um$$

$$N = a\alpha z$$

and

$$a = (4 - \lambda)/6 \qquad b = \tfrac{1}{2}(z - 1)(\lambda + m) \qquad u = \alpha(z - 1)/2.$$

The results for m and λ can be calculated from the equations

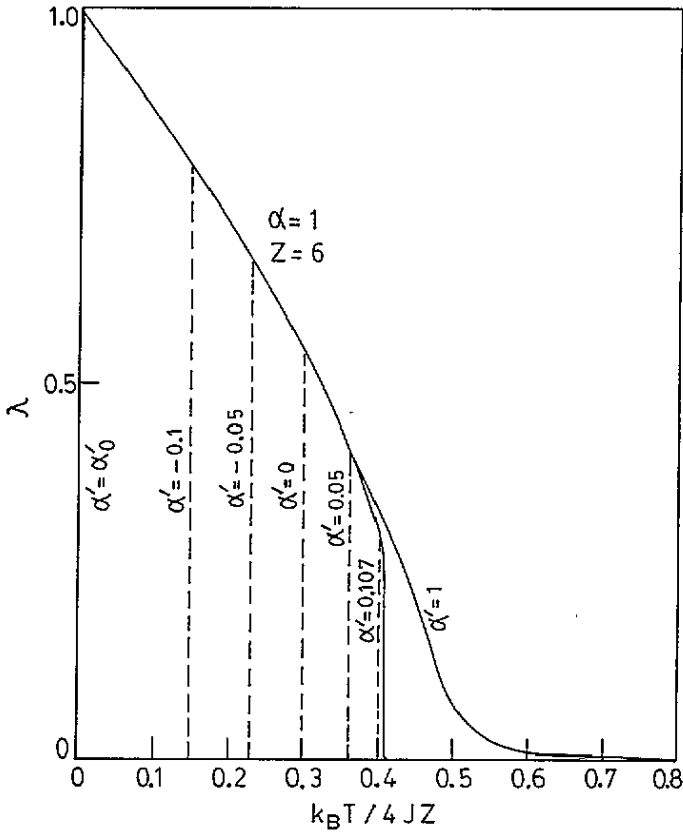$$m = \lambda(1 + 2y) \tag{13}$$

$$1/\lambda = 1 + 3y + 3y^2 \tag{14}$$

Figure 2. The quadrupolar ordering parameter λ plotted against $k_B T/4Jz$ for $\alpha = 1$, $z = 6$. The curves fall more rapidly than those for m do.

where

$$y = \frac{1}{N} \sum_k [\exp(\beta \omega_k) - 1]^{-1}$$

with $\beta = 1/k_B T$, k_B being the Boltzmann constant.

The form of ω_k shown by equation (12) cannot be used. Considering only the leading term of the expansion of $f(\gamma_k)$ we obtain the following approximation for ω_k:

$$\omega_k \simeq \omega_0 + 2zJmR(1 - \gamma_k)(1 + \mu\gamma_k) \tag{15}$$

where

$$R = 1 - \tfrac{1}{2}\alpha' + \alpha az + \alpha b + \alpha P \tag{16a}$$

$$\mu = az\alpha/R \tag{16b}$$

$$P = \frac{uP_1 + \alpha'P_2}{\alpha' + a\alpha + 2um} \tag{16c}$$

$$P_1 = a\alpha(\lambda - m) - \alpha'm + \tfrac{2}{3}\alpha'(\lambda + 2) \tag{16d}$$

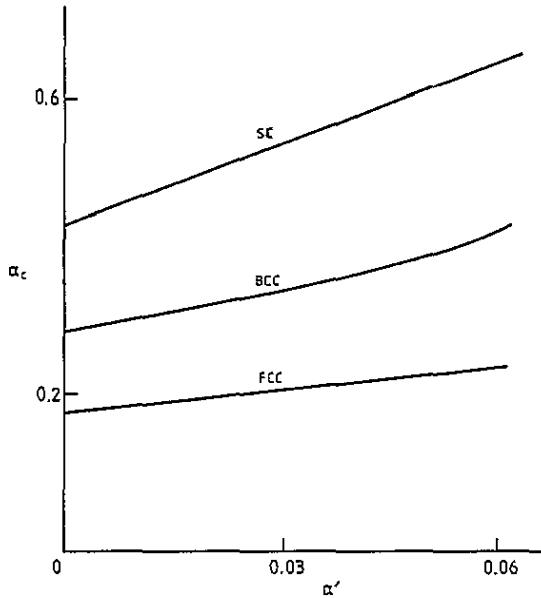$$P_2 = \tfrac{1}{2}[a\alpha + \tfrac{1}{6}\alpha'(8 + \lambda)]. \tag{16e}$$

Figure 3. The variation in critical value of first-order-to-second-order transition α_c with respect to the changes in α' for SC, BCC and FCC lattices.

The results for the Curie temperature T_C can be obtained by taking the limits $\omega_0 \to 0$, $m \to 0$. We obtain

$$\frac{k_B T_C}{Jz} = \frac{4}{3}\frac{R_0}{F_0} \qquad (17)$$

where R_0 and F_0 are the values of R and F at T_C, with

$$F \simeq \frac{I - \mu(I-1)}{1-\mu} \qquad (18)$$

$$I = \frac{1}{N}\sum_k \frac{1}{1-\gamma_k}. \qquad (19)$$

4. Results and discussion

In this section we present a detailed discussion about the thermal variation in m and λ and about some novel features revealed by T_C in the parameter space. In I the case $\alpha' = 0$ was studied and it was seen there that, for α exceeding a certain critical value α_c, the second-order transition becomes first order and that α_c is different for different lattices. α_c may therefore be called a tricritical point. When the biquadratic exchange is included, the essential condition for the existence of a tricritical point remains the same but α_c would then depend sensitively on α'. We have reached this conclusion after a large number of observations on the behaviour of m with temperature for different values of α and α'. Figures 1 and 2 demonstrate the thermal variation in m and λ, respectively, and figure 3
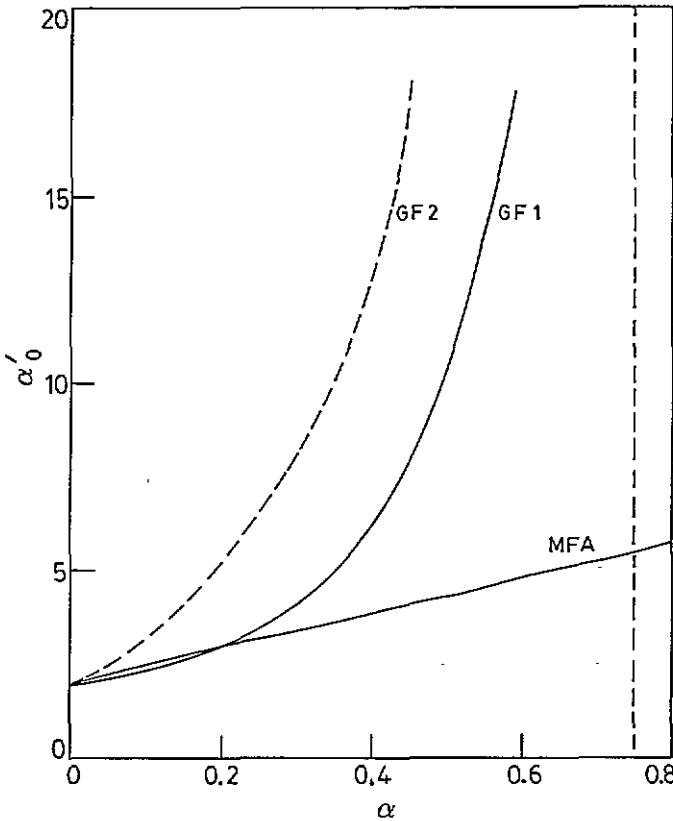
Figure 4. The variation in α'_0 (the critical value of α' where T_C vanishes) with respect to α. The full curve labelled GF 1 is obtained from the condition $F_0 = \infty$ and the broken curve labelled GF 2 is obtained from the condition $R_0 = 0$. The results obtained by Munro and Girardeau are also shown by the curve labelled MFA.

shows the variation in α_c with α' for SC, BCC and FCC lattices. It is seen that, for all lattices, α_c increases with increase in α'. Also, the α_c versus α' curve becomes flatter as z increases.

Before discussing the novel aspects of magnetization curves and the quadrupolar ordering we shall concentrate on another interesting feature of the model considered. We note that the transition temperature vanishes for certain values of α and α'. The result agrees with those obtained from the MFA. However, in the present Green function approach the quantitative results are very different. We note that, for T_C to vanish, one may have $R_0 = 0$ or $F_0 = \infty$. The former condition yields

$$\alpha'^2(\tfrac{2}{3}\alpha - \tfrac{1}{2}) + \alpha'[1 - \tfrac{1}{3}\alpha + \tfrac{2}{3}\alpha z + \tfrac{2}{3}\alpha^2(z-1)] + \tfrac{2}{3}\alpha(1 + \tfrac{2}{3}\alpha z) = 0 \qquad (20)$$

and the latter yields

$$\alpha'^2(\tfrac{2}{3}\alpha - \tfrac{1}{2}) + \alpha'[1 - \tfrac{1}{3}\alpha + \tfrac{2}{3}\alpha^2(z-1)] + \tfrac{2}{3}\alpha = 0. \qquad (21)$$

We have therefore four roots of α'. However, two of these are unphysical. These roots arise from the negative sign before the discriminant. The reason that these are unphysical is that these roots give $\alpha'_0 = 0$ for $\alpha = 0$. Such a point in the parameter space is meaningless
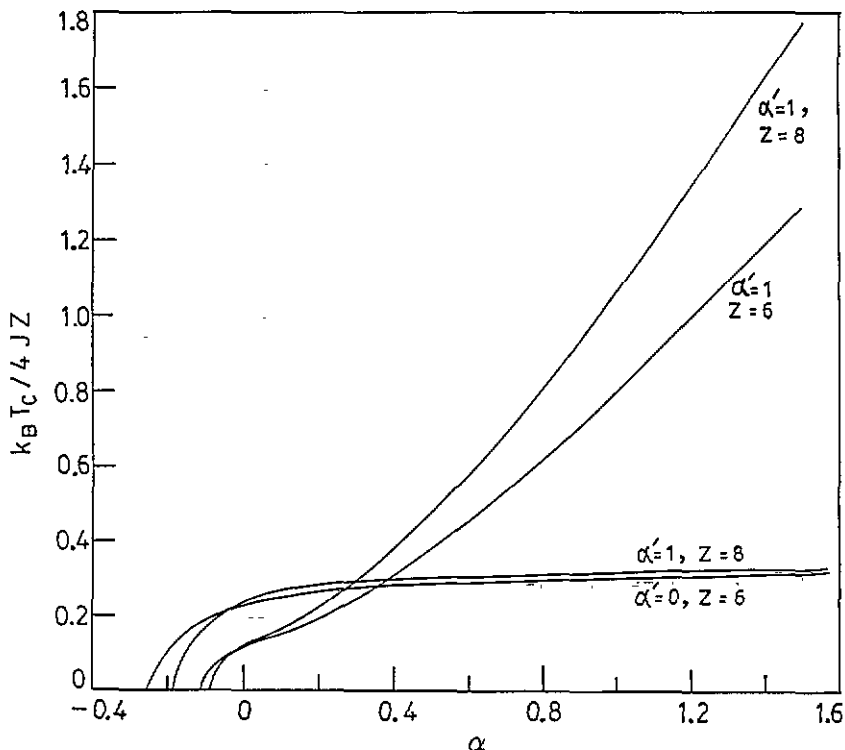
Figure 5. The variation in $k_B T_C/4Jz$ with respect to α for $\alpha' = 0$ and 1 and $z = 6$ and 8.

since this would correspond to a simple Heisenberg model. Considering the other two roots, we have plotted α'_0 against α in figure 4. Two curves are obtained: one for $F_0 = \infty$ and the other for $R_0 = 0$. The latter curve deviates more than the former compared with the MFA curve. For small values of α, the values of α'_0 obtained from the former agree with those of the MFA. The marked difference from the MFA result is seen from the fact that α'_0 goes to infinity at $\alpha = 0.75$ in both cases, while the MFA does not yield such a restriction. Furthermore, it has been found that, in the vicinity of α'_0 obtained from $R_0 = 0$, one finds a short range where an isolated first-order transition occurs, which is absurd. So, we concentrate only on the $F_0 = \infty$ condition which yields a broad range around α'_0 where a first-order transition occurs followed by a second-order transition. These are discussed in more detail in the following paragraph.

    To begin with, we would like to point out one interesting feature. The condition $F_0 = \infty$ as stated above yields, for $z = 6$, $\alpha = 1$, the result $\alpha'_0 = -0.1678$ where T_C vanishes. In the computation of m for the same values of z, α and α' we note that m is double valued at $T_C = 0$: one value is $m = 0$ and the other $m = 1$. This establishes the validity of the condition $F_0 = \infty$. For several other values of α', m has been computed and the results are shown in figure 1. The case $\alpha' = \alpha'_0$ is indicated by the thick line on the ordinate. As α' is increased from α'_0 to $\alpha'_c = 0.107$, m remains double valued at T_C. These are indicated as broken lines while the case for α'_c is shown as a full curve suggesting the onset of a second-order transition. The criterion for the order of transition which we are using is that, for a second-order transition, m is single valued everywhere and is zero at T_C, having no solution beyond T_C. The criterion for a first-order transition is that m is double valued
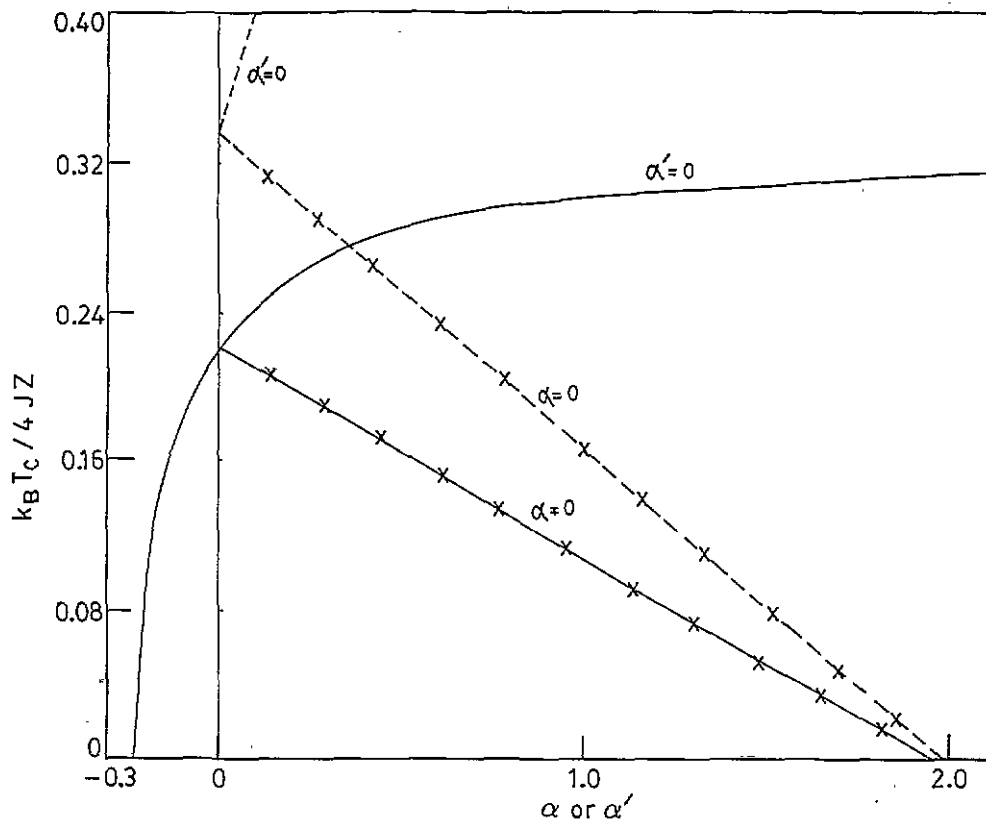
Figure 6. Competition between α and α': $k_B T_C/4Jz$ plotted against α (or α'), keeping α' (or α) fixed. The full curve without crosses represents the results for $\alpha' = 0$ and the full curve with crosses represents the results for $\alpha = 0$. These are compared with the corresponding MFA results shown as broken curves with and without crosses.

everywhere, even beyond T_C, but at $T > T_C$ a bulge occurs, the curve extending to a certain extent and going to zero at T_C. A better criterion should have been used by expanding m in powers of m, i.e. $m = am + bm^2$, etc, but in the present case, owing to enormous analytical complexities, it is very difficult to write m in the form of such an expansion.

Figure 2 represents the nature of the variation in λ with respect to $k_B T/4Jz$. The qualitative nature of the variation is identical with that of m. Also, λ goes to zero at T_C along with m for all cases. These results indicate that no separate quadrupolar phase exists. However, in the case of the first-order transition the magnitude of discontinuities is much less than for m for specific values of α and α' and for a particular lattice structure. Therefore, the ferromagnetic ordering of spins almost completely dominates the quadrupolar ordering at temperatures just below T_C.

The variation in $k_B T_C/4Jz$ with respect to α for $\alpha' = 0, 1$ and $z = 6, 8$ are shown in figure 5. The qualitative natures of variation for both these lattices are identical. For $\alpha' = 0$, T_C first increases sharply from zero and then increases very slowly, approaching ultimately the asymptotic MFA value. For $\alpha' = 1$, T_C always increases sharply for both the lattices.

Figure 6 demonstrates the competition between the three-atom exchange and biquadratic

exchange. The values of $k_B T_C/4Jz$ are plotted against α (or α'), keeping α' (or α) fixed. The full line with the crosses represents the variation in $k_B T_C/4Jz$ with respect to α' (three-atom exchange is absent) and the full line represents the variation in $k_B T_C/4Jz$ against α (biquadratic exchange is absent). The broken line with the crosses and the broken line represent the corresponding MFA results.

5. Concluding remarks

In the preceding sections some novel aspects of a modified Heisenberg ferromagnet have been studied within the framework of the RPA Green function equation-of-motion method. It is not possible at present to point out precisely the compounds where the present Hamiltonian is exactly valid. However, there exist some hexagonal insulators with chemical formula ABX_3 where both biquadratic exchange and three-atom exchange might be believed to be present. A typical example of an ABX_3-type compound is $CsMnBr_3$ where Mn is the magnetic atom. Mn atoms form linear chains along the hexagonal c axis and form a triangular lattice in the basal a–b plane, giving rise to three-atom exchange, associated with a biquadratic exchange. The mechanism which gives rise to these exchange processes is not of course obvious and is the subject of our future investigations (Gaulin *et al* 1989, Johnson *et al* 1979).

Furthermore, it is important to mention two aspects: usually in reality the present Hamiltonian should correspond to antiferromagnets or complex spin structures and one should consider the sublattice structure for realistic evaluation of the physical quantities; secondly, since we have considered the spin-1 model, no question of partial alignment of spins arises. In future investigations we shall study the higher-spin cases.

Finally, we would like to point out that both the qualitative and the quantitative results are extremely sensitive to the estimation of F. Here we have considered only the leading term. In addition to this, since we are discussing the statistical effects of higher-order exchange processes, the other terms of the expansion of spectral function y should also be included.

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