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Determination of Magnetic Ordering in Heisenberg Magnets from High-Temperature Expansions

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We investigate the possibility of determining the type of magnetic ordering to be expected for a Heisenberg model by using high-temperature expansion methods. (The latter have been addressed in the past only to questions about the model *given* the type of ordering.) We take as a criterion for the critical temperature T_c that the static correlation function $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ becomes long range as the critical temperature is approached from above. This criterion is applied by looking for the "generalized Fourier amplitude" λ_α of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ that will diverge at a finite temperature. This "generalized Fourier amplitude" is essentially like the usual Fourier amplitude—for Bravais lattices it is precisely the latter, and it is suitably generalized for lattices with more than one spin per unit cell. In the special case where ferromagnetism is expected, the divergent λ_α is essentially the susceptibility. In general, the divergent λ_α is to be estimated by extrapolation from the first terms of its expansion in powers of T^{-1}, in the spirit of the usual high-temperature expansion methods. This approach has been applied to normal spinels with nearest neighbor AB and BB interactions. Our preliminary results suggest that the approach will give reasonably definitive answers to the question of the type of ordering to be expected. Furthermore, they suggest that correlation corrections to the predictions of molecular-field theory can have a very large effect on the qualitative properties of the model, i.e., the type of ordering. The possible relevance of these results to the problems of $CoCr_2O_4$ and $MnCr_2O_4$ is mentioned.

IT was first suggested by Kramers[1] and Opechowski[1] that by studying the high-temperature expansion for the zero-field susceptibility per particle $\chi(T)$, one could estimate the Curie temperature by utilizing the definition of T_c, namely, $\chi(T) \to \infty$ as $T \to T_c$. Also involved in obtaining this information is the *estimation* (by extrapolation) of the general term of the series from the knowledge of the first few terms of the series, which are calculated explicitly for a given model Hamiltonian (e.g., Ising or Heisenberg models). Since then, many studies along these lines have been made.[2] These studies have been addressed essentially to the following questions: Given the type of magnetic ordering (ferromagnetic or antiferromagnetic), what is the location of the critical temperature T_c, and how do various thermodynamic functions behave near T_c? The purpose of the present paper is to investigate the possibility of using a similar approach for determining the *type* of order to be expected for a given model Hamiltonian. We will be concerned here only with the Heisenberg model $H = \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$, although the approach is easily generalized.

We first seek a criterion which will enable us, in principle, to determine the ordering at $T = T_c$. To this end we make use of the essential physical fact that as $T \to T_c$ from above, the correlation $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \text{trace } \mathbf{S}_i \cdot \mathbf{S}_j \exp(-\beta H)/\text{trace} \exp(-\beta H)$ becomes long range.[3] This is equivalent to the divergence to ∞ of $\chi(T)$ for a ferromagnet, as may be seen intuitively from the fact that $\chi(T)$ is proportional to $\phi(T) \equiv N^{-1} \sum_{ij} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ (N = number of sites i).[4] However, for an antiferromagnet $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ should alternate in sign as j changes, so that even for long-range correlations, $\phi(T)$ might not diverge—indeed one sees that it will not, since $\chi(T)$ is finite for an antiferromagnet. On the other hand, $\phi'(T) = N^{-1} \sum_{ij} c_i^* c_j \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ *would* be expected to $\to \infty$ if $c_j = +1$ or -1 on sites that were "up" or "down" in the ordered state that will occur for T immediately below T_c.[5] Furthermore, the divergence of ϕ' in this case has the desirable property that it truly reflects the long-range character of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ rather than resulting artificially from some property of the c_i. If a more complicated ordering should occur, e.g., a spiral with wave vector $\mathbf{k}_0$, then $\phi'(T)$ would be expected to $\to \infty$ if one chose $c_i = \exp(i\mathbf{k}_0 \cdot \mathbf{R}_i)$.

These considerations lead to the following criterion applicable to general interactions J_{ij}. Let

$$\phi(c, T) \equiv N^{-1} \sum_{ij} c_i^* c_j \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle / \bar{S}_i \bar{S}_j, \tag{1}$$

with the c_i constrained by

$$\sum_i |c_i|^2 = N. \tag{2}$$

The function $\phi(c, T)$ is clearly very similar to the $\phi'(T)$ discussed above—the only difference is that we have now used, mainly for convenience, the normalized correlation $s_{ij} = \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle / \bar{S}_i \bar{S}_j$, where $\bar{S}_i^2 = S_i(S_i+1)$, S_i being the spin quantum number for the ith site. Likewise, for an infinite system $\phi(c, T)$ should approach

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[1] H. A. Kramers, Leiden Supplement No. 83, 1936 (unpublished). W. Opechowski, Physica **4**, 181 (1937); **6**, 1112 (1938).

[2] For example, C. Domb, Advan. Phys. **9**, 149 (1960); G. S. Rushbrooke and P. J. Wood, Mol. Phys. **6**, 409 (1963).

[3] Leon Van Hove, Phys. Rev. **95**, 1374 (1954); R. J. Elliott and W. Marshall, Rev. Mod. Phys. **30**, 75 (1958).

[4] To see this, consider for simplicity a Bravais lattice (one spin per primitive unit cell), so that $\phi(T) = \Sigma_j \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$. Since $|\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle| \leq S(S+1)$, where S is the spin quantum number, $\phi(T) \to \infty$ only if $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ does not $\to 0$ too rapidly with the distance between sites. For a ferromagnet, $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is expected to be positive, so that when it is long ranged, $\phi(T)$ indeed does blow up (for an infinite system, of course).

[5] This criterion is similar to the divergence of the staggered susceptibility recently employed by Rushbrooke and Wood (see Ref. 2) for determining T_c in simple antiferromagnets.

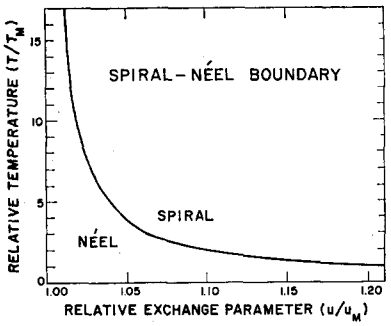

FIG. 1. Spiral–Néel boundary for $\tilde{c}_{n\nu}$ in the third approximation.

infinity as $T\to T_c$ if the coefficients c_i are chosen so as to maximize (1) at all temperatures $T>T_c$, subject to (2). It will be shown elsewhere[6] that, in essence, these particular c_i uniquely determine the type of order at the Curie point.

As is well known, the set of c_i that maximize (1) subject to (2), namely, $\tilde{c}_i$, is the eigenvector of S_{ij} with maximum eigenvalue: $\sum_j S_{ij}\tilde{c}_j=\lambda_{\max}\tilde{c}_i$. The solution of this eigenvector problem is usually tractable, the essential difficulty occurring in the calculation of S_{ij}.

Our procedure is to calculate S_{ij} as a power series in $\beta=1/kT$. Letting $S_{ij}^{(r)}$ be the sum of this series up to order β^r, we then determine $\tilde{c}_i^{(r)}$, the rth approximation to $\tilde{c}_j$, as the maximum eigenvector of $S_{ij}^{(r)}$. This gives $\tilde{c}_j$ as a power series in β, and so leads to $\phi(\tilde{c}, T)$ as a power series in β. The critical temperature T_c and $\tilde{c}(T_c)$ are then estimated by extrapolation from the first few terms in the spirit of the usual approaches.[2] Comparing with molecular-field theory, we find that *in the first approximation, our present approach yields precisely the same results as the molecular-field approximation* (MFA) both for T_c and the type of ordering $(\tilde{c}_i)$. This is convenient since the MFA is the true "single-spin" approximation, and so any corrections to it represent true correlation effects.

An initial investigation of the applicability of this approach has been made to a few examples. The most interesting of these is the normal cubic spinel with nearest-neighbor A–B and B–B interactions. The eigenvectors are of the form $c_i\to c_{n\nu}=c_\nu\exp(i\mathbf{k}\cdot\mathbf{R}_{n\nu})$, where $n\nu$ now labels a site, n refers to the unit cell, and $\nu=1, \cdots, 6$ corresponds to the six sites per cell. We have calculated $S_{n\nu,m\mu}^{(r)}$ and the maximum eigenvectors $\tilde{c}_{n\nu}^{(r)}$, for $r\leq 3$.

[6] T. A. Kaplan, H. E. Stanley, K. Dwight and N. Menyuk (to be published).

The results are partially summarized in Fig. 1, where temperature, normalized to the molecular field critical temperature T_M, is the ordinate and u/u_M is the abscissa. u_M is the value of $u\equiv 4J_{BB}S_B/3J_{AB}S_A$, such that the MFA predicts a Néel-type ordering at $T=T_M$ for $u<u_M$, but a spiral ordering for $u>u_M$.[7] In our present formalism, the Néel configuration corresponds to a maximum eigenvector with $k=0$, whereas the maximum eigenvector for a spiral has a nonzero $\mathbf{k}$. It turns out that the maximum eigenvector $\tilde{c}_{n\nu}^{(1)}$ will be independent of T, but of course will depend on the J_{ij}. Thus, the left-hand edge of Fig. 1 comprises a *vertical* boundary: $\tilde{c}_{n\nu}^{(1)}$ corresponds to a Néel state to the left of it, and to a spiral to the right. In higher order this boundary becomes modified. Only the boundary obtained in third-order is shown in Fig. 1; the second-order boundary is similar for $u/u_M\gtrsim 1.07$, lying somewhat below the third-order curve. Since the true critical temperature is expected to be below T_M, it is seen that u_c, the true critical value of u, will be much greater than u_M if the true boundary lies above or near the third-order boundary. Since our three approximations to this boundary move successively to higher T for fixed u, they indeed do suggest that one can expect to have Néel ordering at T_c for values of u much greater than that predicted by molecular-field theory. In other words, these results *suggest that correlation effects can have a very large effect on such qualitative predictions of the model as the type of ordering.*

This suggestion can be strengthened only if more terms are obtained and certain convergence questions considered. Such work is in progress. Nevertheless, it is interesting to examine the case of $CoCr_2O_4$, for which $u/u_M=0.9$ as determined by neutron diffraction at 4.2°K.[8] Here the variations with temperature of the net magnetization and of the fundamental neutron diffraction peaks predicted by MFA are all in good agreement with experiment. However, the MFA predicts a Néel-to-spiral transition at 0.9 T_c, whereas experimentally no coherent satellite peaks exist above 0.3 T_c. Thus the MFA has apparently overestimated the spiral stability by the MFA, as indeed is indicated by the theory presented above. Consequently, our present results give the promise that correlation effects, properly considered, will provide an understanding of the magnetic properties of this material. Similarly, it is hoped that they may also be of value in connection with the problem of $MnCr_2O_4$.[6,9]

[7] D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, Phys. Rev. **126**, 540 (1962).
[8] N. Menyuk, K. Dwight, and A. Wold, J. Phys. **25**, 528 (1964).
[9] T. W. Houston and A. J. Heeger, Phys. Letters **10**, 29 (1964).