ior of T_1 and T_2, and predicts the magnitude and functional dependence of $1/T_1$ and the magnitude of $1/T_2$. It is not sufficiently refined to predict the ratio of $(1/T_2)/(1/T_1)$. Although studies of adsorbed molecules on surfaces could furnish similar information, the results depend sensitively on molecular coverage, substrate homogeneity, magnetic impurities, and broken surface bonds.[18] These difficulties are absent in the intercalation complexes since in this case the two-dimensional character of the molecular species is a *bulk* rather than a surface property.

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Magnetic Order in the Heisenberg Model

Robert H. Swendsen
Institut für Festkörperforschung der Kernforschungsanlage, Jülich, West Germany
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The molecular-field approximation (MFA) and the random-phase approximation (RPA) are shown to be unreliable in predicting the types of order in cubic Heisenberg magnets that include second-neighbor exchange. Anomalies in the Padé-approximant critical temperatures are found and traced to instabilities in the RPA and MFA. These instabilities lead to new types of order involving canted and perpendicular alignment of the spins.

The usual catalog of ordered states in cubic Heisenberg magnets with first- and second-neighbor exchange was originally obtained in the molecular-field approximation (MFA).[1-4] The random-phase approximation (RPA)[5-7] included spin waves in the description of the magnetization process and improved the estimates of the critical temperatures, but gave the same types of magnetic order. Refined approximations and exact limiting cases have usually been restricted to nearest-neighbor exchange and the simplest types of order, and have failed to produce any significant changes in the basic picture. However, several aspects of this picture are unreliable and substantial changes are needed.

An indication that something essential is missing from the RPA can be found in certain anomalies that we shall point out in the Padé-approximant values of the critical temperatures. All such anomalies can be traced to instabilities or near instabilities in the RPA, and can be explained by assuming regular corrections to the

RPA magnon energies. These corrections lead to new types of magnetic order that involve canted and perpendicular alignment of the spins, and allow specific predictions of anomalies to be made for cases in which the Padé results are not yet available.

The most accurate and reliable estimates of the critical temperatures are obtained from a Padé-approximant analysis of the exact high-temperature expansions of the magnetic susceptibilities. This method has been applied to a wide range of spins and exchange constants in cubic lattices,[8-12] and its results can be directly compared with the RPA results. Such comparisons show that the RPA values are generally quite good (usually well within 10%). In addition, for nearest-neighbor exchange, the differences between the Padé and the RPA results follow a definite pattern. As Tahir-Kheli[13] has pointed out, the formula

$$T_C = T_C^{\mathrm{RPA}}\{1 + \tfrac{1}{3}(1 - 1/S)[1 - 1/F(-1)]\}, \qquad (1)$$

where $F(-1)$ is the appropriate Watson integral,[14] provides a very good fit to the Padé results for ferromagnets. The Néel temperatures for simple nearest-neighbor antiferromagnets are somewhat higher than the corresponding Curie temperatures, but Eq. (1) is still good.[8] Note that $T_C > T_C^{\mathrm{RPA}}$ for high spins and $T_C < T_C^{\mathrm{RPA}}$ for spin $\frac{1}{2}$, with the corrections for $S=\infty$ and $S=\frac{1}{2}$ being equal in magnitude and opposite in sign.

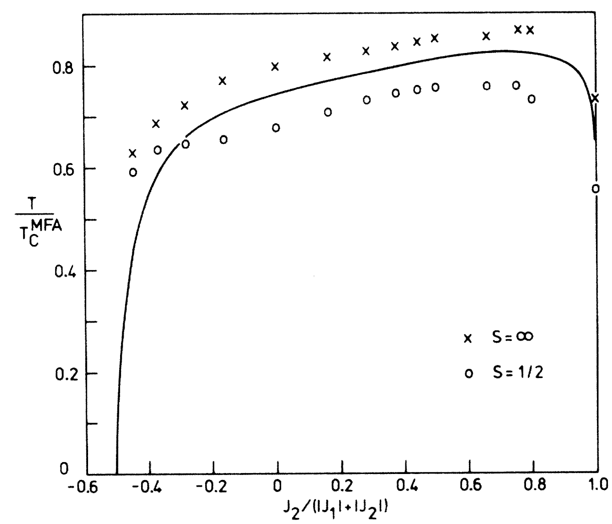

FIG. 1. Comparison of Padé-approximant values for the Curie temperatures (Refs. 9, 10, and 15) with the RPA (solid curve for all spins) for an fcc ferromagnet with first- and second-neighbor exchange.

When positive second-neighbor exchange is included for ferromagnets, the corrections to T_C^{RPA} remain regular and uniform, as shown in Fig. 1 for the fcc ferromagnet. [I have divided T_C by T_C^{MFA} to remove the $S(S+1)$ spin dependence, and have plotted it against $J_2/(|J_1|+|J_2|)$ to include all values of the exchange constants in one graph.] When J_2 is negative, the Padé values for infinite spin continue to be shifted uniformly upward. However, an anomaly appears for spin $\frac{1}{2}$; the correction changes sign when J_2 is close to $-J_1$ and the points lie above the RPA curve.

The simple cubic (sc) type-I and bcc type-I antiferromagnets behave similarly to the ferromagnets, but all other antiferromagnets that have been investigated by the Padé method show very large anomalies. Figure 2 shows the situation for fcc type-I order. For spin $\frac{1}{2}$, $T_C < T_C^{\mathrm{RPA}}$ only when $J_2 > 1.5|J_1|$. When J_2 is small, the corrections become positive and *large* ($T_N^{\mathrm{Padé}} = 0.52 \times T_N^{\mathrm{MFA}}$ when $J_2 = 0$, while $T_N^{\mathrm{RPA}} = 0$).

The anomalies can be traced to instabilities or near instabilities in the RPA, which appear as magnons with zero (or small) energy, but a nonzero wave vector. When corrections to the RPA lower the energy of these critical magnons, the usual order becomes unstable. This can also be seen from the MFA, where the instabilities show up as cancelations in the effective magnetic fields that link certain sublattices. The critical RPA magnons have an energy proportional to these effective fields and rotate the sublattices with respect to each other.

It is natural to seek corrections to the RPA within the Green's-function formalism. In fact,

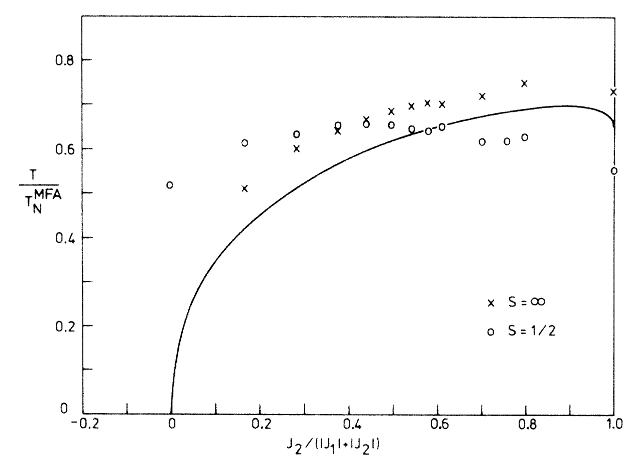

FIG. 2. Same as Fig. 1 for an fcc type-I antiferromagnet.

the anomalous behavior has been seen in the modified Callen decoupling scheme[16,17] and will be reported elsewhere.[18] The modified Callen decoupling results indicate that the anomalies can be understood from the following simple qualitative arguments.

To predict the phase transitions and the appearance of anomalies, we need to know the qualitative behavior of the corrections. For nearest-neighbor ferromagnets, we have seen that the corrections are positive (support the magnetic order) near the critical temperature for spin greater than 1 and negative (oppose the magnetic order) for spin $\frac{1}{2}$. On the other hand, we know from Dyson's work[15] that the corrections support the order for all spins at low temperatures by eliminating the negative T^3 term in the magnetization predicted by the RPA.[19] Consequently, we would expect the corrections for high spins to be positive at all temperatures, but to change sign when $S=\frac{1}{2}$, being positive at low temperatures and becoming negative as the temperature is raised.

If this spin and temperature dependence holds for all usual types of magnetic order, the usual order will always be stable at low temperatures. For high spins, the usual order will continue to be stable at high temperatures, and no anomalies will be seen. All Padé results substantiate this prediction by showing a uniform positive shift in the high-spin critical temperatures.

To discuss spin $\frac{1}{2}$ in detail, we shall use renormalization factors to describe the corrections. These factors are different for different contributions to the energy (or effective fields) and depend on the relative alignment of the interacting spins as well as their separation. We will use a factor R_{pi} for the ith-neighbor exchange between parallel spins and a different factor, R_{ai}, when the spins are antiparallel.

First consider the fcc ferromagnet in a renormalized MFA. The interactions within a (111) plane give an effective field

$$H_{\text{eff}}{}^{111}=2\sigma J_1 6R_{p1}, \tag{2}$$

where $\sigma=\langle S_z\rangle$. This maintains ferromagnetic order within the (111) plane whenever $J_1>0$. The total effective field includes interactions between (111) planes:

$$H_{\text{eff}}{}^{\text{tot}}=H_{\text{eff}}{}^{111}+2\sigma J_1 6R_{p1}+2\sigma J_2 6R_{p2}. \tag{3}$$

As long as J_2 is positive, ferromagnetic order is stable and the only effect of the renormalization factors is the usual uniform shift of the Curie temperatures. However, if J_2 is negative, the sum of the last two terms in Eq. (3) can also be negative. Ferromagnetic order is then unstable and the system can lower its energy by rotating the (111) planes. In terms of a remormalized RPA, the energy of the critical magnons is proportional to the sum of the last two terms in Eq. (3). When this energy becomes negative, ferromagnetic order is destroyed.

If the R's are all equal to unity, as is usually assumed, ferromagnetism is only unstable when $J_2\leq -J_1$. If they differ from unity and oppose the magnetic order, ferromagnetic order will be destroyed for some value of $J_2>-J_1$. The new order will be determined by the dependence of the renormalization factors on the angle between interacting spins and will probably involve a canted alignment with a nonzero, macroscopic magnetic moment. However, the essential feature is that the corrections that destroyed ferromagnetic order will stabilize the new alignment of spins. Consequently, the critical temperatures (transition to the disordered phase) will be shifted upward for $S=\frac{1}{2}$ when J_2 is near $-J_1$ (as is actually seen in Fig. 1). Since the corrections stabilize ferromagnetism at low temperatures, we have two phase transitions; the system goes from the ferromagnetic to the canted to the paramagnetic state as the temperature is raised.

Since the canted state appears at some definite value of the ratio J_2/J_1, a plot of the critical temperature should show a kink at this point. Unfortunately, there are not enough Padé values available to really test this prediction, although the values shown in Fig. 1 are consistent with a change of slope when $J_2\approx -0.1J_1$ (this would, of course, mean that the renormalization effect is quite large).

Fewer points are available for the bcc ferromagnet, but the anomaly is present and consistent with this analysis. No data are available for negative values of J_2 in the sc ferromagnet with spin $\frac{1}{2}$.

For sc type-I and bcc type-I antiferromagnets, nearest-neighbor exchange joins different magnetic sublattices, while all next-nearest-neighbor exchange stays within a sublattice. The analysis is identical to that for the corresponding ferromagnets and the same anomalies are predicted. Unfortunately, no Padé results are available.

In fcc type-I order ($J_1<0$, $J_2>0$), the spins within a (100) plane are parallel to each other and antiparallel to the spins in the adjoining (100) planes. If we consider two sublattices, each consisting of alternate (010) planes, the effective field arising from interactions within a (010) sublattice is

$$H_{\mathrm{eff}}{}^{010} = -2\sigma J_1 4R_{a1} + 2\sigma J_2 6R_{p2}, \tag{4}$$

which supports antiferromagnetic order within the (010) sublattices. The total field is

$$H_{\mathrm{eff}}{}^{\mathrm{tot}} = H_{\mathrm{eff}}{}^{010} + 2\sigma J_1 4(R_{p1} - R_{a1}). \tag{5}$$

The net interaction between (010) sublattices depends only on J_1 and vanishes when $R_{p1} = R_{a1}$. The relative ordering of the (010) sublattices is thus determined entirely by the sign (not the magnitude) of the net corrections.

For spin $\frac{1}{2}$, the second term in Eq. (5) becomes negative as the temperature is raised, destroying type-I order. If the R's are monotonic functions of the angle between spins, the new stable configuration is characterized by the perpendicular alignment of spins on different (010) sublattices. Again, the new magnetic order is stabilized by the same corrections that destroyed type-I order. Since the second term in Eq. (5) is proportional to J_1, we expect it to dominate the net shift in the critical temperatures when J_2 is small ($T_C > T_C{}^{\mathrm{RPA}}$). However, when J_1 is small, the system is composed of weakly coupled sc ferromagnets and the critical temperatures show the normal downward shift associated with R_{p2}. The Padé results have precisely this behavior (as shown in Fig. 2), with the crossover occurring for $J_2 \approx 1.5|J_1|$.

The analysis of the remaining antiferromagnets is similar. For fcc type-II and bcc type-II order, the instability again arises from a cancelation of the nearest-neighbor interactions. We again predict an anomalous, positive shift in the critical temperatures for spin $\frac{1}{2}$ when $|J_2|$ is relatively small, and a crossover to the normal negative shift when $|J_2| \gg |J_1|$. The anomaly is present in the Padé results for both lattices.

Type-IIIA order in an fcc antiferromagnet only occurs when both J_1 and J_2 are negative and $J_2/J_1 \leq \frac{1}{2}$. The anomaly for spin $\frac{1}{2}$ should again be present as a result of a cancelation of nearest-neighbor interactions, but it should always be positive. The critical temperatures have not yet been located by the Padé method.

For type-II and type-III orders in sc antiferromagnets the instabilities arise from a cancelation of both first- and second-neighbor interactions. The requirement for stability is

$$|J_1|(R_{p1} - R_{a1}) - 2|J_2|(R_{p2} - R_{a1}) > 0. \tag{6}$$

The anomaly for spin $\frac{1}{2}$ is expected to be positive for all values of the exchange constants for both types of order. The Padé method has not yet been applied to these antiferromagnets.

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