Induced-moment singlet-triplet model: Relationship between the ground-state moment and the critical temperature

S. Jafarey, Yung-Li Wang, and K. Rauchwarger
Department of Physics, Florida State University, Tallahassee, Florida 32306
(Received 31 July 1978)

Using the critical temperatures estimated by the high-temperature-series-expansion (HTSE) technique and the ground-state moment calculated in the constant-coupling approximation (CCA) we show a plot of the latter versus the former. An excellent agreement is found between our prediction and the experimental observations on Pr_3Tl under a hydrostatic pressure and perhaps on $Pr_{3-x}La_xTl$. We also show that while the values of the critical temperatures in the CCA are generally much improved, the ground-state moment versus critical-temperature behavior predicted in CCA is as poor as that in the mean-field approximation. We emphasize that the correct behavior of the variation of T_c with the crystal-field to the exchange-interaction ratio near the critical value of this ratio is the decisive factor in explaining the experimental observations.

I. INTRODUCTION

In the preceding paper[1] we have obtained a very accurate estimation of the critical temperature T_c for the induced-moment singlet-triplet model. We showed that T_c computed in the molecular-field approximation (MFA) is totally unacceptable for systems with the crystal-field to the exchange-interaction ratio close to the critical value required for a magnetic ordering. In this paper we shall show that neither is the MFA result for the ground-state moment (zero-temperature magnetization) acceptable in this situation. More importantly, we shall try to understand the discrepancies between the molecular-field predictions and the experimental observations about the critical-temperature–spontaneous-moment relationship for Pr_3Tl diluted[2] with La and Pr_3Tl under a hydrostatic pressure.[3]

Pr_3Tl is perhaps the most extensively studied induced-moment system in recent years. The exchange-interaction to the crystal-field ratio $\mathcal{J}/\Delta$ of the compound is only slightly greater than the critical value for having a magnetic ordering at all. Consequently, the critical temperature of the compound is very low, $T_c = 12°\,K$, as compared to the crystal-field splitting between the crystal-field ground level Γ_1 and the first excited level Γ_4, $\Delta = 77°\,K$. Also, the ground-state moment is only $0.7\mu_B$ (Bohr magneton) as compared to $3.2\mu_B$ of a free ion. Pr_3Tl is thus an ideal system for studying the induced-moment magnetism.

To study the onset of the induced-moment magnetization, Andres *et al.*[2] introduced a small quantity of nonmagnetic La ions into Pr_3Tl and found that replacing 7 at.% of Pr with La in the pure compound could actually drive the system subcritical. Alternatively, it has been observed by Guertin *et al.*[3] very recently, that a hydrostatic pressure can vary the ratio of the crystal field to the exchange interaction and lower the critical temperature to zero at a pressure of about 8 kbar. This latter one has the advantage of using the same pure compound thus avoiding the complications associated with the mixed crystals. Both groups have measured the critical temperatures and the spontaneous moments as the ratio $\mathcal{J}/\Delta$ varies. A plot of the ground-state moment versus the critical temperature was made in each experiment. The general behavior is that the ground-state moment rises almost linearly as the critical temperature increases. This is in striking contrast with the molecular-field approximation prediction which shows a much slower rise of the ground-state moment, and thus a much too small moment for the whole range of T_c, and a concave upward curve.

An immediate question which arises is whether the observed behavior is due to a physical process not included in the Hamiltonian used to describe the system, or whether the molecular-field approximation is simply too crude to be used here. Obviously, one should try to answer the second part of the question before attempting the first part. We have obtained the values of T_c as a function of $\Delta/\mathcal{J}$ accurately in the preceding paper.[1] We need an accurate estimation of the ground-state moment as $\Delta/\mathcal{J}$ varies. We shall attempt to accomplish this by using the constant-coupling approximation in this paper.

The constant-coupling approximation has been applied to the induced-moment systems by Cooper[4] and by Wang and Cooper[5] to obtain the critical value of the $\Delta/\mathcal{J}$ ratio for magnetic ordering at zero temperature. McPherson and Wang[6] have computed further, for a singlet-singlet model, the critical temperature and the ground-state moment as functions of $\Delta/\mathcal{J}$. They show that the critical temperatures computed in the constant-coupling approximation are fairly accurate compared with values obtained in the high-temperature series expansion and that the ground-state moment is greatly reduced from the MFA values for $\Delta/\mathcal{J}$ near the critical value. While the accuracy of the results in the constant-coupling approximation is difficult to assess and varies from one system to the other, the fact that the critical value of $\Delta/\mathcal{J}$, for magnetic ordering at $T=0$, calculated by the constant-coupling approximation[4] for the singlet-triplet model, is only 2% off from the value given by our HTSE estimation, has motivated our calculation of the ground-state moment using the same approximation. In Sec. II we show the CCA calculations of the ground-state moment and the critical temperature. A discussion of the reliability of such calculations will be presented in Sec. III, where we also discuss the ground-state moment versus the critical-temperature behavior of $Pr_{3-x}La_xTl$ and that of Pr_3Tl under a hydrostatic pressure.

II. CONSTANT-COUPLING APPROXIMATION

The Hamiltonian of the singlet-triplet induced-moment system has been given in Eq. (2) of the preceding paper.[1] The singlet and triplet wave functions at vanishing molecular field are also given in Eqs. (3)–(6) of Ref. 1. The basic formulation in the constant-coupling approximation for this model has been given by Cooper,[4] who was interested in the paramagnetic susceptibility and the critical value of $\Delta/\mathcal{J}$ (for $T=0$) and, therefore, treated the effective-field term as a perturbation in the calculations. We need both the critical temperature and the ground-state moment for each value of the $\Delta/\mathcal{J}$ ratio. While the former can be obtained in Cooper's approach, the latter requires a treatment of the effective-field term exactly.

We shall recapitulate Cooper's approach in the following and refer the details of the calculation to his paper.[4] In the constant-coupling approximation (CCA), the magnetization is computed in two ways. The single-ion Hamiltonian is assumed to take the form

$$\mathcal{H}_1 = V_c - zhJ^z \ , \tag{1}$$

where V_c is the crystal-field potential giving rise to the singlet-triplet energy scheme (with other higher-lying states ignored), and zh is an effective field due to the z nearest-neighbor moments. The thermal average $\langle J^z \rangle$ can be easily calculated as a function of h and will be denoted by $\langle J^z \rangle_1$.

Next we consider the two-ion Hamiltonian, which is

$$\mathcal{H}_2 = \mathcal{H}_{20} + \mathcal{H}_2^1 \ , \tag{2}$$

$$\mathcal{H}_{20} = V_{c1} + V_{c2} - 2\mathcal{J}\vec{J}_1 \cdot \vec{J}_2 \ , \tag{3}$$

$$\mathcal{H}_2^1 = -(z-1)h(J_1^z + J_2^z) \ . \tag{4}$$

Here $\mathcal{J}$ is the exchange parameter defined in Ref. 1. $\mathcal{H}_2$ can be diagonalized if needed and $\langle J^z \rangle$ can be computed, although this is a little more involved. The value of $\langle J^z \rangle$ will again be a function of h, and will be denoted by $\langle J^z \rangle_2$. To determine h, one demands that $\langle J^z \rangle_1 = \langle J^z \rangle_2$.

Cooper[4] has given the 16 wave functions and energy eigenvalues of $\mathcal{H}_{20}$. They are denoted as $|\alpha_n\rangle$ and ν_n in his paper. To calculate the critical temperature, we calculate $\langle J^z \rangle_1$ and $\langle J^z \rangle_2$ for an infinitesimal h. Thus the effective field terms in $\mathcal{H}_1$ and $\mathcal{H}_2$ can be treated perturbatively. This simplifies the computation greatly. We can easily show that T_c is given by solving the equation

$$\sum_{\substack{n,m \\ (n \neq m)}} \frac{2\zeta_{nm}^2}{\nu_n - \nu_m} \frac{\exp(-\beta_c \nu_m)}{\sum_l \exp(-\beta_c \nu_l)} + \beta_c \sum_n \zeta_{nn}^2 \frac{\exp(-\beta_c \nu_n)}{\sum_l \exp(-\beta_c \nu_l)} = \frac{2z}{z-1} \frac{4\alpha^2[1-\exp(-\beta_c \Delta)] + \beta_c \Delta \exp(-\beta_c \Delta)}{2\Delta[1+3\exp(-\beta_c \Delta)]} \ , \tag{5}$$

where

$$\zeta_{nm} = \langle \alpha_n | J_1^z + J_2^z | \alpha_m \rangle \ , \tag{6}$$

and m,n are summed over the two-ion eigenstates of $\mathcal{H}_{20}$. We have also used the matrix elements appropriate for Pr^{3+} in a cubic field and $\alpha = \langle 0_c | J^z | 1_c \rangle = (20/3)^{1/2}$. To establish our notation of crystal-field states with that of Cooper's, we note that

$$|0_c\rangle = |\Gamma_1\rangle, \ |1_c\rangle = |\Gamma_{4b}\rangle \ ,$$

$$|2_c\rangle = |\Gamma_{4c}\rangle, \ \text{and} \ |3_c\rangle = |\Gamma_{4a}\rangle \ .$$

To calculate the ground-state moment with the two-ion Hamiltonian, we need to treat $\mathcal{H}_2^1$ exactly. However, we are interested in the ground state of the system which is a linear combination of $|\alpha_1\rangle$, $|\alpha_2\rangle$, $|\alpha_3\rangle$, and $|\alpha_4\rangle$. A diagonalization of a 4×4 matrix gives the wave function of the ground state from which the ground-state moment can be computed. The ground-state moment with the single-ion Hamiltonian is simply given by

$$\langle J^z \rangle_1 = \frac{2\alpha^2 zh}{\Delta}\left[1 + \left(\frac{2\alpha zh}{\Delta}\right)^2\right]^{-1/2} \ . \tag{7}$$

Again, by demanding the ground-state moments calculated with the two Hamiltonians be the same, the effective field h is determined which gives in turn the ground-state moment. We shall present the results of the calculations in Sec. III.

III. DISCUSSION

We show, in Fig. 1, the variation of the ground-state moment with the ratio $\Delta/\mathscr{J}z\alpha^2$, for an fcc lattice ($z=12$, $\alpha^2=\frac{20}{3}$), calculated in the CCA. The MFA values are also shown for comparison. It is clear that the effect of the zero-point fluctuations is small for small values of $\Delta/\mathscr{J}$, where the system has an almost saturated moment. The reduction of the moment becomes significant as $\Delta/\mathscr{J}$ increases, and a great disparity results as the ratio approaches the critical value for magnetic ordering (at $T=0$). The critical value for ordering in CCA is $\Delta/\mathscr{J}z\alpha^2=3.65$ which is 2% higher than the value estimated by the HTSE, $\Delta/\mathscr{J}z\alpha^2=3.58$, while the MFA value is 12% too high. A drawback in the CCA result is the unphysical behavior of the curve at very small values of $\Delta/\mathscr{J}z\alpha^2$. Other similar unphysical results in the CCA and in the Bethe-Peierls-Weiss method (another cluster-effective-field approximation) have been observed before.[7] Fortunately, the values of $\Delta/\mathscr{J}z\alpha^2$ which we are interested in are those close to the critical value and are far away from the region where the approximation breaks down. We should also note that the breakdown of the CCA near $\Delta=0$ may occur because of the singlet-triplet model approximation which ignores all other crystal-field eigenstates. Should all states be retained, $\Delta=0$ would correspond to an isotropic Heisenberg ferromagnet. For such a system Kasteleijn and Van Kranendonk[8] have shown that the CCA gives an unsaturated magnetization at $T=0$, which is unphysical but can be resolved by applying an external field, however small, to the ferromagnet in the calculation.

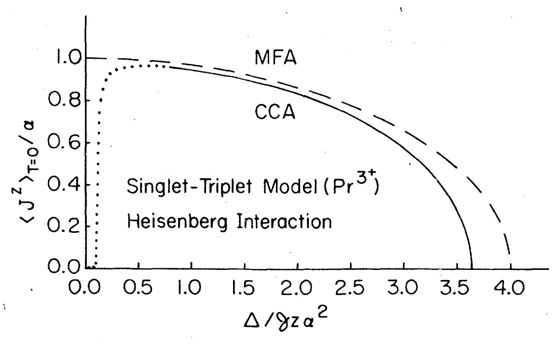

FIG. 1. Normalized ground-state moment $\langle J^z \rangle_{T=0}/\alpha$ vs $\Delta/(\mathscr{J}z\alpha^2)$ in the mean-field approximation (MFA) shown in dashed line and the constant-coupling approximation (CCA) shown in solid line ($z=12$). The critical value of $\Delta/(\mathscr{J}z\alpha^2)$ for the ground-state moment to appear is much reduced in the CCA from its value in the MFA. The dotted portion of the CCA curve is the region where the CCA gives unphysical results.

As emphasized before, our main interest is in the behavior of the induced-moment system as the value of the $\Delta/\mathscr{J}$ ratio approaches the critical value for ordering. Based on the fact that the critical value for ordering calculated in CCA is only 2% away from the HTSE value, we assume that the behavior of the ground-state moment is well described by the CCA near the critical value of $\Delta/\mathscr{J}$. We have also found that if we plot the normalized ground-state moment $\langle J^z \rangle_{T=0}/\alpha$ vs $(\Delta/\mathscr{J})/(\Delta/\mathscr{J})_c$ (i.e., $\Delta/\mathscr{J}z\alpha^2$ normalized to its critical value), the curve of CCA falls on the curve of MFA almost exactly. In other words, the CCA values of ground-state moment can be given fairly accurately by the simple equation,

$$\langle J^z \rangle_{T=0}/\alpha = [1-(\Delta/\mathscr{J})^2/(\Delta/\mathscr{J})_c^2]^{1/2} , \tag{8}$$

suggested by the MFA result. This result is not restricted to the fcc lattice. However, $(\Delta/\mathscr{J})_c$, takes a different value for a lattice of different geometry. The fact that the CCA predicts the same behavior of the ground-state moment near the critical value of $\Delta/\mathscr{J}$ as that by the MFA may simply be a reflection of the effective-field nature of the CCA calculation. It should be of great value to re-examine the behavior of the ground-state moment using a more refined calculation. In this paper we shall content ourselves with the CCA values.

While there is no real need of calculating the critical temperature in the CCA for a discussion of the experimental findings about the ground-state-moment—critical-temperature relationship, we should like to examine the possibility of explaining the behavior using the CCA results alone. The variation of the critical temperature with the $\Delta/\mathscr{J}z\alpha^2$ ratio is shown in Fig. 2 along with the curves given by the HTSE and by the MFA. It is seen that the CCA values are, in general, much more accurate than those of the MFA. However, near the critical value of $\Delta/\mathscr{J}z\alpha^2$ for ordering at $T=0$, the CCA curve shows similar erroneous behavior to that of the MFA; it plunges to zero too rapidly. To compare the behavior of the three curves, we show the plot of $T_c/T_c(\Delta=0)$ vs $(\Delta/\mathscr{J})/(\Delta/\mathscr{J})_c$ in Fig. 3. For $\Delta/\mathscr{J}$ above 95% of its critical value, the range of $\Delta/\mathscr{J}$ appropriate for Pr_3Tl under hydrostatic pressure or with La dilution, the CCA curve almost coincides with the MFA curve, while the HTSE curve shows a quite distinct behavior from the other two; its descent is far less rapid as the critical value is approached. This is indeed the key to understanding the experimental observations of Guertin *et al.*[3] and Andres *et al.*[2]

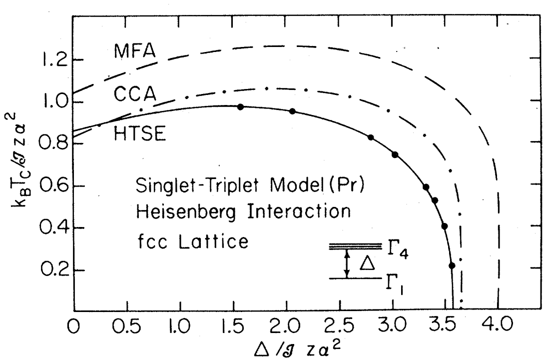

FIG. 2. Critical temperature T_c, in units of $\mathcal{J}z\alpha^2/k_B$ vs $\Delta/\mathcal{J}z\alpha^2$) in the MFA, CCA, and high-temperature series expansion (HTSE).

We now show the ground-state moment versus the critical-temperature plot. In Fig. 4, the solid curve is obtained by using the critical temperatures estimated in the HTSE method,[1] and the ground-state moment calculated in the CCA. It should be noted that each CCA value for the ground-state moment has been chosen for the same value of $(\Delta/\mathcal{J})/(\Delta/\mathcal{J})_c$ as that used for the estimation of T_c/Δ. The dashed curve shows the MFA prediction and the dash-dot curve is the prediction of a collective-excitation (CE) model used by Andres *et al.* Three sets of data are shown. The crosses are taken from Andres *et al.*,[2] who measured $\langle J^z \rangle_{T=0}$ and T_c for a number of compounds $Pr_{3-x}La_xTl$ with $x < 0.07$. The open circles and the solid circles are results of measurements of Guertin *et al.*[3] They were taken by placing Pr_3Tl under a hydrostatic pressure which increases the value of $\Delta/\mathcal{J}$, pushing it towards the critical value. As discussed by Guertin *et al.*,[3] great difficulties were associated with the determination of the ground-state moment. The impossibility of satisfying the criterion $T << T_c$ for pressures near the critical pressure for complete suppression of ferromagnetism and the strong field dependence of the magnetization data at low fields contribute, for the most part, to the uncertainty in the ground-state moment. Two different procedures of extrapolation were used by Guertin *et al.*[3] to determine the ground-state moment from the magnetization versus internal field H_i data. The solid circles in Fig. 4 represent results of extrapolations to $H_i = 0$ from data in the range of $2 \leqslant H_i \leqslant 4$ kOe; the open circles are obtained by using the values of the moment at which the magnetization versus H_i curve first deviates from linearity. Our calculation agrees with the latter set of data extremely well. (The data points at $T_c/\Delta = 0.03$ have error bars of about 0.04 in $\langle J^z \rangle/\alpha$.)[3] MFA or the CE obviously cannot explain the experimental behavior. Neither can the CCA alone be used. In fact, if the values of ground-state moment obtained in the CCA are plotted versus the values of $T_c/T_c(\Delta = 0)$ in the CCA, one obtains exactly the same curve as that of the MFA despite the fact that the CCA values are in general much more accurate than those of MFA. This is because in the "scaled plots": $\langle J^z \rangle_{T=0}/\alpha$ and $T_c/T_c(\Delta = 0)$ vs $(\Delta/\mathcal{J})/(\Delta/\mathcal{J})_c$, the CCA curves coincide with the MFA curves near the critical ratio of $\Delta/\mathcal{J}$ for the magnetic ordering. In the plot of $\langle J^z \rangle_{T=0}/\alpha$ versus T_c/Δ, however, the CCA curve would lie a little higher than that of the MFA because of the lower

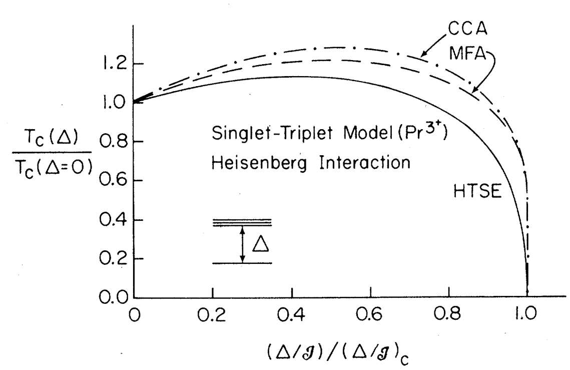

FIG. 3. Critical temperature T_c, normalized to its value for $\Delta = 0$, vs $(\Delta/\mathcal{J})/(\Delta/\mathcal{J})_c$ in the MFA, CCA, and HTSE. Here $(\Delta/\mathcal{J})_c$ is the critical value of $\Delta/\mathcal{J}$ for magnetic ordering to occur at $T = 0$ and is different in the different approximations (MFA, CCA, and HTSE). Note that for $(\Delta/\mathcal{J})$ greater than 0.95 $(\Delta/\mathcal{J})_c$, the MFA and CCA curves almost coincide, while the HTSE curve drops far less rapidly than the MFA and CCA curves. This behavior of the HTSE curve is crucial for a successful explanation of the experimental observations.

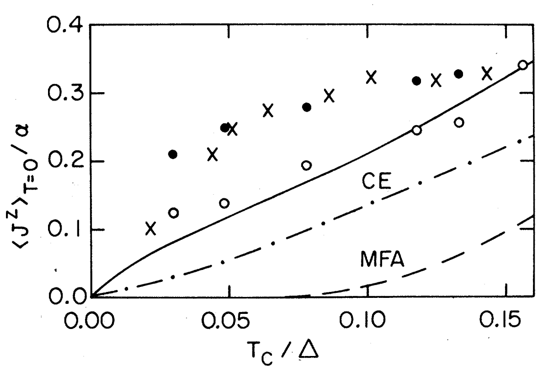

FIG. 4. Ground-state moment $\langle J^z \rangle_{T=0}/\alpha$ vs critical temperature T_c/Δ. The result of the present calculations is shown in the solid curve. Dashed curve represents results of the MFA and the dashed-dotted curve was obtained by including the effects of the simple collective excitations in the system. Three sets of experimental data are shown. Crosses are taken from Andres *et al.*[2] the closed and open circles are from Guertin *et al.*[3]

value of $T_c(\Delta=0)$ in the CCA calculation (Fig. 2); the CCA curve can be obtained by shifting every point on the MFA curve horizontally by 17%. It is, however, as poor as the MFA prediction.

We should also point out that the relationship between the ground-state moment and the critical temperature that we have calculated is a fairly general result. While we have chosen the fcc nearest-neighbor interaction model for our calculations, the result is valid for the other two cubic lattices, sc and bcc. Indeed, the "scaled plots" for the three lattices coincide to a high degree of accuracy. The results should also be fairly accurate for exchange interactions extending to further neighbors, as long as the range of interaction remains short. It is, therefore, not a surprise that our result based on the fcc nearest-neighbor interaction model agrees so well with the observed behavior in the real physical systems, Pr_3Tl under a hydrostatic pressure, and Pr_3Tl diluted with La. Finally, we should remember that the exact behavior of the ground-state moment may have not been described correctly by the CCA near the critical value of $\Delta/\mathcal{J}$ for magnetic ordering. There has been an indication[9] that the ground-state moment vanishes in a power law with a power less than that predicted by the MFA and the CCA [Eq. (8)]; MFA and CCA predict a power of $\frac{1}{2}$. If this is true, we should expect a corresponding higher value for the ground-state moment, and the solid curve shown in Fig. 4 would be raised higher.

IV. ACKNOWLEDGMENTS

This work is supported by the NSF under Grant No. DMR77-21539. We also acknowlege the computer time provided to us by the Florida State University Computer Center.

[1]K. Rauchwarger, S. Jafarey, and Y. L. Wang, Phys. Rev. B 19, 2712 (1979) (preceding paper).

[2]K. Andres, E. Bucher, S. Darack, and J. P. Maita, Phys. Rev. B 6, 2716 (1972).

[3]R. P. Guertin, J. E. Crow, F. P. Missell, and S. Foner, Phys. Rev. B 17, 2183 (1978).

[4]B. R. Cooper, Phys. Rev. 163, 444 (1967).

[5]Y. L. Wang and B. R. Cooper, Phys. Rev. 172, 539 (1968).

[6]J. W. McPherson and Y. L. Wang, J. Phys. Chem. Solids 37, 625 (1976).

[7]J. S. Smart, *Effective Field Theories of Magnetism* (Saunders, Philadelphia, 1966).

[8]P. W. Kasteleijn and J. Van Kranendonk, Physica (Utrecht) 22, 317 (1956); 22, 367 (1956).

[9]P. Pfeuty and R. J. Elliott, J. Phys. C. 4, 2370 (1971).