

## Néel temperature in $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$

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Wertheim *et al.* have carefully measured the Néel temperature of the mixed system of iron and zinc fluorides. Over the concentration range  $0.25 \leq x \leq 1$ , their results show an essentially linear decrease with magnetic concentration of the form  $T_N(x)/T_N(1) = mx + c$ , where parameters  $m$  and  $c$  are approximately the following:  $m \sim 1$  and  $c \sim 0$ . Such a result is in direct contrast with the earlier observations of Baker *et al.* on mixed crystals of manganese and zinc fluorides, where the corresponding choice for the parameters  $m$  and  $c$  would seem to be  $m \sim 5/4$  and  $c \sim -1/4$ . To explain these results we have carried out a coherent-potential-approximation (CPA) analysis which takes into account the relevant exchange interactions (including second-neighbor contributions) and the anisotropy. While for the Mn-Zn system the anisotropy is quite small, for the Fe-Zn system, it is rather large. As such, to treat the latter system we have combined the CPA with the Devlin type of RPA procedure. Our results are in excellent agreement with experiment. Moreover, it appears that the observed differences in the behavior of the two mixed systems are due primarily to differences in their anisotropies.

### I. INTRODUCTION

Wertheim *et al.*<sup>1</sup> reported a careful measurement of the Néel temperature of the mixed system  $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$  some eleven years ago. Their results, measured over a range of concentrations, i.e.,  $1 \geq x \geq 0.25$ , showed an essentially linear decrease of the Néel temperature of the mixed system with approximately a unit slope and no intercept, i.e.,

$$[T_N(x)/T_N(1)]_{\text{Fe-Zn}} \sim x. \quad (1.1)$$

This result was somewhat surprising in view of an earlier experiment<sup>2</sup> by Baker *et al.* on a related mixed system  $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$ , which showed a considerably more rapid rate of decrease with dilution (by nonmagnetic zinc). An approximate representation of the manganese-zinc results would be of the form

$$[T_N(x)/T_N(1)]_{\text{Mn-Zn}} \sim \frac{1}{4}(5x - 1). \quad (1.2)$$

The physical origin of the differences in the observed behavior of the two systems was not understood at the time. This was particularly perplexing since (a) the antiferromagnetic spin configurations are identical and (b) the exchange interactions are qualitatively similar in both the mixed systems.

Recently, we were able to develop a coherent-potential approximation (CPA) for treating random antiferromagnets with exchange interactions of arbitrary range.<sup>3</sup> When such a theory, coupled with a random-phase approximation (RPA), was applied<sup>4</sup> to the mixed system Mn-Zn, its results were found to be in reasonable agreement with the experimental observations of Baker *et al.*<sup>2</sup> Of course, we realize that much cannot be made of any quantitative agreement between such a theoretical treatment and the experiments of Baker

*et al.*<sup>2</sup> because of the following reasons.

First, the CPA—RPA theory<sup>3</sup> itself is only a crude approximation and any of its estimates for  $T_N(x)$  can only be of qualitative value because at times they are in error by a few percent. The situation can, however, be improved somewhat by working with the ratio  $T_N(x)/T_N(1)$ , which is less susceptible to errors associated with the use of the RPA. For such a ratio, the major source of uncertainty is contributed by the errors inherent in our<sup>3</sup> CPA—which are small when  $1 - x \ll 1$  but increase to become of the order of a few percent for  $x < 0.5$ . Indeed, as  $x$  decreases further towards the percolation concentration, these errors become proportionately very large. Secondly, with arbitrary dilution there is uncertainty associated with assigning exchange interactions to a pair of magnetic atoms. While it is possible to make certain guesses as to how the exchange might vary with the introduction of finite amount of dilution by zinc atoms, in the absence of a reliable procedure for doing this, these are likely to be only rough guesses.<sup>5</sup> Thirdly, it might even be argued that the early experiments<sup>2</sup> of Baker *et al.* were in themselves not very accurate because of the difficulty of determining  $T_N(x)$  by the method used by these workers (i.e., by observing the disappearance of the nuclear magnetic resonance lines of the fluorine nuclei as the system temperature is lowered towards  $T_N$ ).

These uncertainties notwithstanding, the agreement between the CPA—RPA theory and the experimental results on  $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$  is, nonetheless, significant. Therefore, it seems in order that the rather different experimental results on  $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$  be analyzed within a similar theoretical format to see whether the differences between

these two systems can be understood. Moreover, because the quality of the experimental results for the Fe-Zn system is believed<sup>6</sup> to be a shade better, it provides a somewhat more severe test of whether our CPA—RPA framework is useful for such an analysis.

To this end, in this paper we formulate the CPA—RPA theory for the Fe-Zn system (Secs. II and III) and compare its results with the experimental results of Wertheim *et al.*<sup>1</sup>(Sec. IV). We find that the theoretical estimates for the behavior of the ratio  $T_N(x)/T_N(1)$  are very close to the corresponding experimental results over a wide range of concentrations, even though the actual value of the Néel temperature itself is predicted to within about 6% or so. In view of the earlier statements, this agreement, without any adjustable parameters, is about as good as can be expected and accordingly we are encouraged in our conjecture that the major physical reason for the observed differences in the behavior of the Mn-Zn and the Fe-Zn mixed systems is the difference in the nature and the size of their respective anisotropies. In this connection, it may be mentioned that while the magnetic anisotropy in the  $Mn_xZn_{1-x}F_2$  system is quite small and is caused predominantly by the weak dipolar interactions (and as such it has, what we shall for convenience call, a two-spin origin), the corresponding anisotropy in the  $Fe_xZn_{1-x}F_2$  is relatively much larger and it has a different physical origin, i.e., it is a crystal-field effect. Moreover, because the crystal field is approximately the same<sup>7-9</sup> for  $FeF_2$  as it is for  $Fe^{2+}$  ions in  $ZnF_2$ , the mixing does not materially change the crystal field experienced by the Fe ions (as such, it is convenient to call it a single spin effect). It is essentially these features—as will become more clear in the later sections—which combine to cause the behavior of  $T_N(x)/T_N(1)$  to differ in the Fe-Zn and the Mn-Zn systems, in the manner observed experimentally.<sup>1,2</sup>

## II. COHERENT-POTENTIAL APPROXIMATION

$FeF_2$  and  $ZnF_2$  are isostructural with a rutile-tetragonal crystal structure shown in Fig. 1. The lattice constants  $a_0$  and  $c_0$  are also approximately the same for the two systems,<sup>1</sup> being respectively equal to 4.6966 and 3.3091 for  $FeF_2$ , and 4.7034 and 3.1335, for  $ZnF_2$ . For simplicity, and convenience, we therefore assume that the mixing occurs uniformly and that the exchange integrals between magnetic ions remain unchanged on dilution. In a similar fashion, because the single-ion crystal-field anisotropy  $D$  is also approximately the same  $ZnF_2$  (as experienced by a  $Fe^{2+}$  ion) in the  $FeF_2$  (Ref. 1) and (Ref. 9) systems (being respectively equal

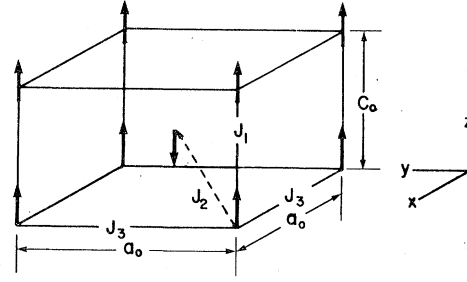


FIG. 1. Antiferromagnetic spin configuration of  $FeF_2$  and the various exchange couplings are shown.

to  $6.46_{-0.10}^{+0.29}$   $cm^{-1}$  and  $7.3 \pm 0.7$   $cm^{-1}$ ), we therefore work with a concentration independent single-ion anisotropy. These two assumptions are clearly approximate in nature and when, in the future, it is necessary to examine any other such physical property of the mixed system where these considerations make a significant quantitative difference, it would certainly be necessary to refine these assumptions. Nevertheless, for the present purposes, this effort is not warranted, for our CPA as well as the RPA are subject to a few percent error—an error which we expect to be similar to that introduced by these assumptions.

For the ground-state magnetic ordering of the Fe-Zn system, shown in Fig. 1, for a given configuration  $\{x\}$ , which specifies the nature of the mixing of the Fe and Zn ions, the system Hamiltonian is

$$\mathcal{H}(\{x\}) = \sum_{i,j} x_i x_j (J_{ij}^{(2)} - J_{ij}^{(1)} - J_{ij}^{(3)}) \times \vec{S}_i \cdot \vec{S}_j - \sum_i x_i D (S_i^z)^2. \quad (2.1)$$

Here  $x_i$ ,  $x_j$  are the occupation operators for the magnetic (Fe) ions, i.e.,

$$(x_i)^2 = x_i; \quad x_i x_j = x_j x_i, \quad (2.2a)$$

$$\bar{x}_i = x \equiv \dots, \quad (2.2b)$$

where the dots denotes relative concentration of Fe ions. (Here a bar at the top indicates a configurational average.) The exchange interactions  $J_{ij}^{(n)}$  are such that

$$J_{ij}^{(n)} = J_{ji}^{(n)} = \begin{cases} J_n, & \text{if the } i \text{ and } j \\ & \text{sites are } n\text{th neighbors} \\ 0, & \text{otherwise.} \end{cases} \quad (2.3)$$

[Note in the Hamiltonian (2.1) we have denoted the couplings  $J_1$  and  $J_3$  to be of intrasublattice variety—i.e., they are ferromagneticlike terms—whereas the coupling  $J_2$  is represented as the intersublattice, i.e., the antiferromagnetic, ex-

change.]

The development of the appropriate CPA equations for the system described by the Hamiltonian  $\mathcal{H}(\{x\})$  falls within the general formulation given by us elsewhere.<sup>3,10</sup> Here, it is important to remember that within such a CPA format, the behavior of the transition temperature is determined entirely by the zero-frequency component of the Green's function, which in turn depends upon the zero-frequency coherent exchange integrals  $j^{(n)}(E=0)$ ,  $n=1, 2, 3$ . In other words, the objective of the CPA is to develop a set of self-consistent equations whose solution gives values of  $j^{(n)}(0)$ , which in turn are to be used in the approximate CPA Hamiltonian,  $\mathcal{H}^{\text{AF}}(0)$ , i.e.,

$$\mathcal{H}^{\text{AF}}(0) = \sum_{i,j} [j_{ij}^{(2)}(0) - j_{ij}^{(1)}(0) - j_{ij}^{(3)}(0)] \times \vec{S}_i \cdot \vec{S}_j - D \sum_i (S_i^z)^2. \quad (2.4)$$

The relevant Néel temperature would then be given by an RPA solution of  $\mathcal{H}^{\text{AF}}(0)$ . [Note that while the  $j^{(n)}(0)$  are renormalized by the system randomness—i.e., they depend on the magnetic concentration  $x$ —the single-ion anisotropy  $D$  is independent of  $x$ .]

We hasten to add that the actual execution of such a program of calculation—namely, the development of the coherent Hamiltonian in the form (2.4) and the obtaining of an RPA solution of such a CPA Hamiltonian *à la* Devlin<sup>11,12</sup>—is nontrivial. Indeed, the procedure has to be embellished considerably beyond what was required for carrying out the corresponding CPA—RPA computations in the  $\text{Mn}_x \text{Zn}_{1-x} \text{F}_2$  system<sup>4</sup> because unlike in Refs. 3, 4, and 10, for the system in hand  $j^{(n)}(0)$  are not invariant with system temperature. It will be recalled that when the anisotropy is absent,<sup>3,10</sup> or when it is a two-spin property and can be adequately decoupled within an RPA so that it renormalizes at least linearly with the system magnetization  $M$ , the functional dependence of  $j^{(n)}(E)$  on  $E$  and the system temperature enters only through the ratio  $E/M$ . [Note that no pathology develops in these cases even when  $T \rightarrow T_c$ .]

It turns out, however, that at any given temperature  $T$  a self-consistent scheme for carrying out the CPA and the RPA can be developed and the corresponding CPA for the zero-frequency coherent exchanges can be written in a format similar to that used in Refs. 3, 4, and 10. We get

$$\frac{x[J_n - j^{(n)}(0)]}{1 + [J_n - j^{(n)}(0)]\Gamma(n)} = \frac{(1-x)j^{(n)}(0)}{1 - j^{(n)}(0)\Gamma(n)}, \quad n=1, 2, 3, \quad (2.5)$$

where

$$\Gamma(n) = \frac{2}{N} \sum_{\vec{k}} \frac{A_{\vec{k}}(n)}{B_{\vec{k}}}, \quad (2.6a)$$

$$A_{\vec{k}}(2) = \rho D + 8j^{(2)}(0)(1 - \gamma_{\vec{k}}^2) + 4j^{(3)}(0)(1 - \nu_{\vec{k}}) + 2j^{(1)}(0)(1 - \eta_{\vec{k}}), \quad (2.6b)$$

$$A_{\vec{k}}(p) = C(\vec{k})[1 - \phi_{\vec{k}}(p)], \quad p=1, 3, \quad (2.6c)$$

$$B_{\vec{k}} = [C(\vec{k})]^2 - [8j^{(2)}(0)\gamma_{\vec{k}}]^2, \quad (2.6d)$$

$$C(\vec{k}) = A_{\vec{k}}(2) + 8j^{(2)}(0)\gamma_{\vec{k}}^2, \quad (2.6e)$$

and

$$\begin{aligned} \nu_{\vec{k}} &= \phi_{\vec{k}}(3) = \frac{1}{2}(\cos 2k_x + \cos 2k_y), \\ \gamma_{\vec{k}} &= \cos k_x \cos k_y \cos k_z, \\ \eta_{\vec{k}} &= \phi_{\vec{k}}(1) = \cos 2k_z. \end{aligned} \quad (2.6f)$$

The parameter  $\rho$  in Eq. (2.6b) is clearly both temperature and anisotropy dependent. For the system with crystal-field single-ion anisotropy being analyzed here,  $\rho$  is, however, equal to  $(2S-1)/2S$  at low temperatures, i.e., at  $T \ll T_c$ . At the transition temperature  $T_c$ , within an Anderson-Callen<sup>13</sup> or a Narath<sup>13</sup> type of decoupling,  $\rho$  is independent of  $D$  and is equal to  $\frac{1}{2}$  or 1, respectively (for the  $S=2$  system). Narath decoupling, however, gives too high a value for the  $T_c$  even for moderately small anisotropies (as compared with the more reliable RPA decoupling<sup>11,12</sup>) and therefore for evaluating the CPA parameters it is not an appropriate starting point. On the other hand, the Anderson-Callen<sup>13</sup> decoupling does a much better job of predicting the  $T_c$  (compare, for example, Refs. 11 and 14). In any event, it turns out that a computational scheme can be designed which converges extremely rapidly to the result that we expect would be obtained by a fully self-consistent CPA—RPA procedure. Such a procedure gives a value of the parameter  $\rho$  at  $T=T_c$  which is weakly dependent on  $D$  and which, according to our estimates for the system in hand, has a value slightly, i.e., a few percent, below 0.5. Any further details of this computational procedure are best deferred until after the RPA has been fully explained. In conclusion, therefore, we need to note only the following: once a procedure for specifying  $\rho$  has been adopted, the solution of the CPA equations for arbitrary  $x$  is straightforward even though it does require numerical computation.

### III. RANDOM-PHASE APPROXIMATION

For a given  $x$ , once  $\rho$  has been specified and a solution for Eqs. (2.5)–(2.6f) has been found, the appropriate  $j^{(n)}(0)$ ,  $n=1, 2, 3$ , are substituted into Eq. (2.4) and in this manner an effective CPA Hamiltonian is obtained. For such a Hamiltonian,

the appropriate RPA is the one proposed by Devlin,<sup>11</sup> which, incidentally, is identical to a decoupling procedure that one of us had arrived at<sup>12</sup> independently of, and prior to, Devlin's work. For the  $S=2$  system under study, the RPA leads to a set of equations which are very cumbersome for the antiferromagnet. Therefore, it is convenient to exploit a simplification which occurs at the transition temperature. It turns out that within the RPA,<sup>12</sup> the numerical value of the antiferromagnetic Néel temperature  $T_N$  for (a two sublattice antiferromagnet) is equal to that of the Curie temperature  $T_C$  of a corresponding (single sublattice) ferromagnet for which the effective Hamiltonian (2.4) is transcribed as follows:

$$\mathcal{H}^F(0) = - \sum_{i,j} [j_{ij}^{(1)}(0) + j_{ij}^{(2)}(0) + j_{ij}^{(3)}(0)] \times \vec{S}_i \cdot \vec{S}_j - D \sum_i (S_i^z)^2. \quad (3.1)$$

[It will be noted that the ferromagneticlike couplings—i.e., terms involving  $j_{ij}^{(1)}(0)$  and  $j_{ij}^{(3)}$ —are the same in Eqs. (2.4) and (3.1), whereas the antiferromagnetic coupling  $j_{ij}^{(2)}(0)$  originally between spins belonging to opposite sublattices is now replaced by an equal but opposite coupling between the same type of spins.]

Now using the procedure published by Devlin,<sup>11,12</sup> after some straightforward but tedious algebra we finally get the following four coupled equations for  $T_C(x)$  of the given effective Hamiltonian (3.1) with  $S=2$ :

$$4 - \frac{1}{6} Z_2 = Q(1), \quad (3.2a)$$

$$16.8 + Z_2 - 0.1Z_4 = Q(2), \quad (3.2b)$$

$$\frac{1}{8}(42 - Z_3) = Q(3) + R(3), \quad (3.2c)$$

$$\frac{1}{8}(306 - 5Z_3) = Q(4) + R(4), \quad (3.2d)$$

where

$$Q(n) = \frac{1}{N} \sum_k \frac{P_n(E_1) - P_n(E_2)}{2[(E_1)^2 - (E_2)^2]}, \quad n=1, 2, 3, 4, \quad (3.3a)$$

$$P_n(E_\alpha) = \tau_\alpha N^{(n)}(E_\alpha)/E_\alpha, \quad \alpha=1, 2, \quad (3.3b)$$

$$\tau_\alpha = \coth[E_\alpha/2k_B T_C(x)], \quad (3.3c)$$

$$N^{(1)}(E_\alpha) = (E_\alpha)^2 D Z_2 + (Z_4 - 10Z_2) D^3, \quad (3.3d)$$

$$N^{(2)}(E_\alpha) = (E_\alpha)^2 Z_4 - 9Z_2 D^3, \quad (3.3e)$$

$$N^{(3)}(E_\alpha) = (E_\alpha)^2 [3\Delta_\alpha Z_2 + Z_3 D - 6Z_2 L(0)] + \Delta_\alpha D^2 (Z_4 - 10Z_2) + 18D^3 + 2D^2 L(0) (10Z_2 - Z_4). \quad (3.3f)$$

$$N^{(4)}(E_\alpha) = (E_\alpha)^2 [3Z_4 \Delta_\alpha + 10D Z_3 - 18D - 6Z_4 L(0)] - 9[Z_2 D^2 \Delta_\alpha + D^3 Z_3 - 2Z_2 L(0) D^2], \quad (3.3g)$$

$$R(p) = \frac{1}{N} \sum_k [(E_1)^2 - (E_2)^2]^{-2} \times \{ [\tau_2 U^{(p)}(E_2) - \tau_1 U^{(p)}(E_1)] (\Delta_1 - \Delta_2) + [(E_1)^2 - (E_2)^2] [V^{(p)}(E_2) - V^{(p)}(E_1)] \}, \quad p=3, 4, \quad (3.3h)$$

$$U^{(3)}(E_\alpha) = (E_\alpha)^3 Z_2 + E_\alpha (Z_4 - 10Z_2) D^2, \quad (3.3i)$$

$$U^{(4)}(E_\alpha) = (E_\alpha)^3 Z_4 - 9E_\alpha Z_2 D^2, \quad (3.3j)$$

$$V^{(p)}(E_\alpha) = \left( \frac{\Delta_\alpha U^{(p)}(E_\alpha)}{k_B T_C(x)} \right) \frac{\exp[E_\alpha/k_B T_C(x)]/E_\alpha}{\{\exp[E_\alpha/k_B T_C(x)] - 1\}^2}, \quad (3.3k)$$

$$\Delta_\alpha = \{ [8L(0) - 2L(\vec{K})] (E_\alpha)^2 + 20[L(K) - 2L(0)] D^2 + DL(K)[4Z_2 L(0) - Z_3 D] \} \times \{ 4(E_\alpha)^2 + 2[Z_2 L(\vec{K}) - 10D] D \}^{-1}, \quad (3.3l)$$

$$L(\vec{K}) = 2j^{(1)}(0)(1 - \eta_{\vec{K}}) + 8j^{(2)}(0)(1 - \gamma_{\vec{K}}) + 4j^{(3)}(0)(1 - \nu_{\vec{K}}). \quad (3.3m)$$

We readily notice that Eqs. (3.2a)–(3.2d) are invariant under the transformation  $E_\alpha \rightarrow -E_\alpha$ ,  $\alpha=1, 2$ . It is sufficient, therefore, to specify  $(E_\alpha)^2$ , which has two solutions given by the quadratic

$$(E_\alpha)^4 + (E_\alpha)^2 [Z_2 L(\vec{K}) - 10D] D + L(\vec{K}) (Z_4 - 10Z_2) D^3 + 9D^4 = 0. \quad (3.4)$$

The set of four equations, (3.2a)–(3.2d), determines the four unknowns,  $k_B T_C(x)$ ,  $Z_2$ ,  $Z_3$ , and  $Z_4$ , in terms of the coherent exchange parameters  $j^{(n)}(0)$ ,  $n=1, 2, 3$  and the anisotropy  $D$ . Because the  $j^{(n)}(0)$  are themselves implicit functions of the magnetic concentration  $x$ —as specified by the CPA equations—this procedure gives us the Curie temperature  $T_C(x)$  of the equivalent ferromagnet. [Note that the auxiliary parameters  $Z_2$ ,  $Z_3$ , and  $Z_4$  are of no physical consequence in the present context, in spite of the fact that a self-consistent solution determines them concurrently with  $T_C(x)$ .]

Here, it is instructive first to look at the behavior of the transition temperature  $T_C$  as a function of the size of the anisotropy  $D$ . In order to avoid confusion with concentration dependence, we shall denote this dependence by  $T_C\{D\}$ . Because the effective anisotropy (within the present model) does not change with randomness, while the effective exchange parameters do, it is helpful to examine how—when randomness is gradually increasing and as a result the effective (coherent) exchange couplings are decreasing in magnitude—the transition temperature for the given system would renormalize with the ratio of the sizes of the anisotropy and the effective exchange couplings.

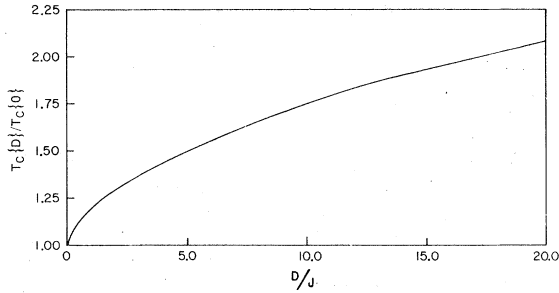


FIG. 2. For the antiferromagnetic system shown in Fig. 1, with  $J_1 = J_3 = 0$  and  $J_2 = J$ , the ratio of the RPA estimates for the Néel temperatures with finite anisotropy,  $T_c\{D\}$  and vanishing anisotropy  $T_c\{0\}$  is given as a function of  $D/J$ .

Because we need only a qualitative answer to this question, we assume only a single effective exchange parameter  $J$  [here we put, for simplicity,  $J_1 = J_3 = 0$ ;  $j^{(2)}(0) \equiv J$ ]. The results for the  $S = 2$  system for the ratio  $T_c\{D\}/T_c\{0\}$  are plotted as a function of  $D/J$  in Fig. 2. We note that when  $D/J$  is of the order of 2 say, this ratio is only about 1.25, whereas when  $D/J$  becomes of the order of 15~20, this ratio increases to about 2. What this means is that for finite  $D$  when  $J$  renormalizes down due to dilution, the actual transition temperature does not go down linearly with  $J$  (which it would have in the absence of anisotropy). This effect would cause different rates of renormalizations for the transition temperatures of the Fe-Zn and the Mn-Zn systems. There is also, of course, another physical effect which impinges on the final result. This relates to how rapidly  $J$  itself renormalizes in the presence of anisotropy. It turns out that within our CPA, for any given choice of  $\rho$  the magnitude of the slope  $dJ/dx$  decreases when  $D/J$  is increased. Here it should be mentioned that, as for the limit  $D \rightarrow 0$ , when  $D \rightarrow \infty$  the renormalization of the transition temperature again becomes proportional to  $J$  and therefore only the latter of the two effects is then present. For the intermediate  $D/J$  limits, however, both these processes of  $T_c$  renormalization contribute and it is therefore necessary to carry out the two sets of numerical computations defined by the CPA Eqs. (2.5) and the RPA relations (3.2a)–(3.2d).

#### IV. SELF-CONSISTENT COHERENT-POTENTIAL APPROXIMATION-RANDOM-PHASE APPROXIMATION

As mentioned in Sec. II, in systems with crystal-field single-ion anisotropy, the confluence of the CPA and the RPA theories is not as simple to achieve as it is in systems where either the anisotropy is absent or where the anisotropy renormalizes simply with the magnetization  $M$ , at least as

fast as the first power of  $M$ . Moreover, it was implied in Sec. II that an appropriate procedure involved the introduction of a renormalization parameter  $\rho$  in the anisotropy terms in the Green's function equations of motion. Here we shall discuss this procedure quantitatively and thereby give a prescription for specifying the renormalization parameter  $\rho$ .

Let us assume that in the equation of motion, of say  $S_b^+$ , the anisotropy dependent term, arising from the relevant commutator, i.e.,

$$[S_b^+, \mathfrak{H}^{AI}(0)]_- \rightarrow D(2S_b^z - 1)S_b^+, \quad (4.1)$$

may be decoupled as follows:

$$(2S_b^z - 1)S_b^+ \sim \rho^2 M S_b^+, \quad (4.2)$$

where

$$M = \langle S_b^z \rangle. \quad (4.3)$$

Clearly, at  $T = 0$  this is feasible for then we have (exactly for the ferromagnet and reasonably accurately for the antiferromagnet)

$$\rho(T) = (2S - 1)/2S, \quad T = 0. \quad (4.4)$$

Such a possibility was also explored in Lines<sup>14</sup> work several years ago and although his own version of the decoupling turned out to be more complicated, he noted that the Anderson-Callen decoupling<sup>13</sup> fitted into this scheme with

$$\lim_{D \rightarrow 0} \rho(T) - 1 = \langle (S_b^z)^2 \rangle - S(S+1)/2S^2, \quad (4.5a)$$

which at  $T \rightarrow T_c$  becomes

$$\rho(T) = (2S - 1)/3S. \quad (4.5b)$$

Moreover, the result for the transition temperature that Lines<sup>14</sup> obtained by using his own decoupling was only a few percent lower (for moderate  $D$ ) than that he computed from the decoupling given in Eq. (4.5b).

Now, the most satisfactory decoupling for treating the crystal-field anisotropy problem is neither the Lines decoupling nor the decoupling given in Eq. (4.5a). Rather, it is the RPA decoupling first published by Devlin.<sup>11,12</sup> Unfortunately, however, the Devlin type of RPA is not convenient for using with the CPA—as indeed is also the case with the Lines version of the decoupling.

Therefore, we attempt an alternative approach. We first compute the  $T_c\{D\}/T_c\{0\}$  using the proper, Devlin RPA (see Fig. 2). Then, for any given  $D$ , we invert the problem and compute the appropriate  $\rho(T_c)$  which would give this same answer. All this, of course, we do only for the nonrandom case. But what we find is encouraging for such a phenomenological  $\rho(T_c)$  turns out to be mostly within about 10% of the Anderson-Callen estimate (4.5b)

TABLE I. The coherent exchange integrals  $j^{(n)}(0)$  are listed for two different choices of the decoupling parameter  $\rho$  and four different magnetic concentrations  $x$ . Note these parameters correspond only to the case A which is explained in Table II and, moreover, that they are given in degrees Kelvin.

$\rho$	$x$	$j^{(1)}(0)$	$j^{(2)}(0)$	$j^{(3)}(0)$	$D$
$\frac{3}{4}$	1.00	0.035	2.62	-0.139	9.61
$\frac{3}{4}$	0.75	0.026	1.834	-0.105	9.61
$\frac{3}{4}$	0.50	0.017	1.104	-0.070	9.61
$\frac{3}{4}$	0.25	0.0086	0.473	-0.036	9.61
$\frac{1}{2}$	1.00	0.035	2.62	-0.139	9.61
$\frac{1}{2}$	0.75	0.026	1.816	-0.105	9.61
$\frac{1}{2}$	0.50	0.017	1.066	-0.070	9.61
$\frac{1}{2}$	0.25	0.0087	0.431	-0.036	9.61

for moderately large  $D/J$ .

Next, we turn our attention to the really central question here: namely, how rapidly do the CPA parameters,  $j^{(m)}(0)$ , vary with changes in  $\rho(T_C)$ . For answering this question we have carried out the computation of the CPA Eqs. (2.5)–(2.6f) using first the zero temperature expression for  $\rho(T)$ , (4.4), which gives for  $S = 2$ ,  $\rho(0) = \frac{3}{4}$ , and next the Anderson-Callen expression which gives  $\rho(T_C) = \frac{1}{2}$ . These results indicate that even though  $\rho$  is changed by as much as 50%, the resultant changes in the CPA parameters are miniscule. (For brevity we append in Table I only a fraction of these results that we have looked at, i.e., for the typical case A as defined in Table II.) Therefore, quite clearly, because the value of  $\rho(T_C)$  which is correctly self-consistent with the proper RPA result<sup>11,12</sup> for the  $T_C$  will be within about 15% or so of the Anderson-Callen result for  $\rho(T_C)$ , i.e.,

TABLE II. The exchange parameters for  $\text{FeF}_2$  determined by Hutchings *et al.* are tabulated in degrees Kelvin. The cases A, B (i), etc., are identified in Ref. 7. The listed  $T_C(1)$  is the parameter free RPA (Refs. 11 and 12) computation for the Néel temperature using the appropriate set of exchange parameters. The listed value for  $D$  is that identified as  $D_{\text{ours}}$  in Eq. (5.1) in the text.

Case	$D$	$J_1$	$J_2$	$J_3$	$T_C(1)$
A	9.61	0.035	2.62	-0.139	83.3
B (i)	9.94	0.053	2.57	-0.114	83.0
B (ii)	9.44	-0.009	2.68	-0.150	84.3
B (iii)	9.79	0	2.60	0	84.9
C	9.98	0	2.52	0	83.3

$\rho = \frac{1}{2}$ , we can expect only very small eventual changes in  $j^{(m)}(0)$  from the results obtained by using the value  $\frac{1}{2}$  for  $\rho(T_C)$ . Indeed, we can reasonably expect that for  $x \sim 0.50$  the final results for  $T_C$  will be within about 1%–3% of those obtained by using  $\rho = \frac{1}{2}$ . [For  $x \geq 0.25$ , the fully self-consistent results can be expected to be those given in Table III, with an error uncertainty which is about one-third of the difference between the corresponding results in Tables III and IV.]

## V. RESULTS

Hutchings *et al.*<sup>7</sup> have given several sets of results for the magnetic parameters, i.e., the exchange integrals and the anisotropy, of the  $\text{FeF}_2$  system. Differences between the different sets arise because of the procedures used for analyzing the neutron-scattering results (from which the spin-wave dispersion is computed). For details of their analyses we refer the reader to their work.<sup>7</sup> Here it suffices to record only the five sets of parameters that they have given. In this regard, we keep their notation and call these sets: A, B(i), B(ii), B(iii) and C, respectively. The relevant parameters are tabulated in Table II.

Our results for the ratio  $T_C(x)/T_C(1)$ , which use the various exchange parameters given in Table II and employ the extremely crude decoupling parameter  $\rho(T_N) \sim \rho(T=0) = \frac{3}{4}$ , are displayed in Fig. 3 as a function of the concentration  $x$  of the Fe ions. In Table II, for convenience, we have also given

TABLE III. Using the Anderson-Callen type of decoupling parameter for the initial CPA computations, i.e.,  $\rho = \frac{1}{2}$ , the ratio of the critical temperatures,  $T_C(x)/T_C(1)$  given by the use of Devlin (Refs. 11 and 12) type of RPA, is listed as a function of the magnetic concentration. Results are listed for the cases A, B (i), B (ii), B (iii) and C, which are identified in Table II.

$X$	A	B (i)	B (ii)	B (iii)	C
1.00	1.0000	1.0000	1.0000	1.0000	1.0000
0.95	0.9481	0.9486	0.9477	0.9487	0.9491
0.90	0.8963	0.8973	0.8955	0.8974	0.8982
0.85	0.8446	0.8460	0.8434	0.8463	0.8473
0.80	0.7930	0.7949	0.7914	0.7952	0.7966
0.75	0.7415	0.7439	0.7396	0.7442	0.7459
0.70	0.6902	0.6930	0.6880	0.6934	0.6954
0.65	0.6391	0.6424	0.6366	0.6428	0.6451
0.60	0.5884	0.5920	0.5855	0.5924	0.5950
0.55	0.5379	0.5419	0.5347	0.5423	0.5452
0.50	0.4879	0.4922	0.4845	0.4926	0.4957
0.45	0.4384	0.4429	0.4348	0.4433	0.4466
0.40	0.3895	0.3941	0.3857	0.3945	0.3979
0.35	0.3412	0.3458	0.3374	0.3462	0.3497
0.30	0.2934	0.2981	0.2897	0.2984	0.3018
0.25	0.2462	0.2506	0.2427	0.2509	0.2542

TABLE IV. This Table is similar to Table III with the only difference that here  $\rho$  was chosen to have the zero temperature value, i.e.,  $\rho = 3/4$ . We estimate that the properly self-consistent results will be close to those given in Table III with an error the size of which will be less than about 1/3 of the difference between the results listed in Table III and the corresponding results given in Table IV.

X	A	B (i)	B (ii)	B (iii)	C
1.00	1.0000	1.0000	1.0000	1.0000	1.0000
0.95	0.9494	0.9498	0.9490	0.9498	0.9502
0.90	0.8988	0.8998	0.8981	0.8998	0.9005
0.85	0.8485	0.8499	0.8473	0.8499	0.8510
0.80	0.7982	0.8001	0.7968	0.8001	0.8015
0.75	0.7482	0.7505	0.7464	0.7505	0.7523
0.70	0.6985	0.7011	0.6963	0.7011	0.7032
0.65	0.6489	0.6520	0.6465	0.6519	0.6543
0.60	0.5997	0.6031	0.5970	0.6030	0.6056
0.55	0.5508	0.5546	0.5479	0.5543	0.5573
0.50	0.5023	0.5063	0.4992	0.5060	0.5092
0.45	0.4542	0.4584	0.4509	0.4580	0.4613
0.40	0.4065	0.4108	0.4031	0.4104	0.4138
0.35	0.3592	0.3635	0.3558	0.3630	0.3664
0.30	0.3122	0.3163	0.3088	0.3159	0.3192
0.25	0.2652	0.2690	0.2620	0.2686	0.2718

the result for the transition temperature of the undiluted  $\text{FeF}_2$  system that our RPA procedure yields for given set of parameters. In comparison with the measured value<sup>1</sup>—which is 78.2 °K—the RPA estimate for  $T_C(1)$  is generally seen to be about 6%–8% in error. This in itself is not such a bad estimate. However, as mentioned in the introduction, the error contributed by the RPA to the ratio  $T_C(x)/T_C(1)$  can be expected to be somewhat more modest.

The results displayed in Fig. 3 are seen to be very reasonable—being, for example, only a few percent higher than the experimental results for  $x \sim 0.5$ . These are, however, not yet the final results because they make use of a very crude decoupling parameter.

Next, we refine these results by using the more accurate decoupling parameter of the Anderson-Callen type: namely,  $\rho(T_C) = \frac{1}{2}$ . On the scale used in Fig. 3, these latter results would be indistinguishable from the experimental results. It is, therefore, more useful to show them separately in Table III. As explained, in the preceding section, the properly self-consistent CPA—RPA procedure would eventually yield results which would be very slightly lower than these. For  $x \geq 0.25$ , we estimate that the difference between the final results and those given in Table III would be about one-third the difference between the present results and those obtained by using the very

crude decoupling  $\rho = \frac{3}{4}$  (see Table IV). Therefore, we are led to the conclusion that the CPA—RPA procedure of the present paper yields results for the ratio  $T_C(x)/T_C(1)$ , which are seemingly “identical” to the experimental results of Wertheim *et al.*

Another remark which should be made here is that Hutchings *et al.*<sup>7</sup> have also estimated the dipolar contribution  $\Psi_0^d$  to the anisotropy. Because this contribution is only about 10% of the total anisotropy, and besides the procedure for estimating it is not entirely rigorous, we have absorbed it in the total value of  $D$  through the relation

$$(2S-1)D_{\text{ours}} = (2S-1)D_{\text{Ref. 7}} + \Psi_0^d. \quad (5.1)$$

If the separation between these two types of anisotropies turns out to be really valid even at  $T \sim T_C$ , then our present procedure would at first seem to be subject to another few percent error—especially for larger concentrations. The apparent reason for this would be the fact that  $\Psi_0^d$  should scale down approximately linearly with  $x$  (because it is a two-spin effect). However, in the final

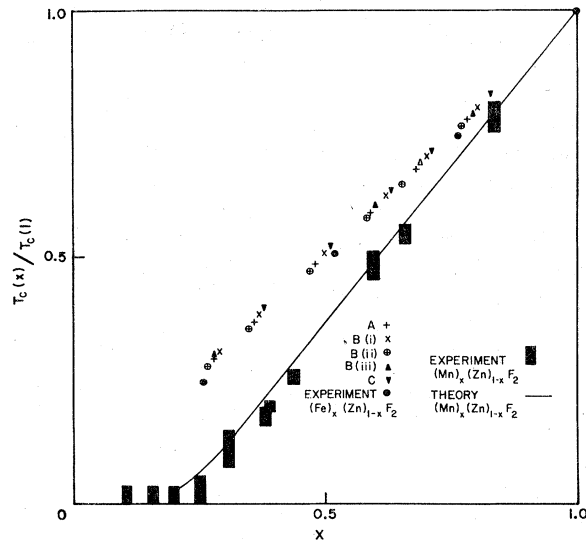


FIG. 3. Results for the CPA—RPA estimates for the Néel temperature of  $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$ , i.e.,  $T_C(x)$ , are for a crude choice of the decoupling parameters, i.e.,  $\rho = 3/4$  given as a function of the magnetic concentration  $x$  for several different sets of exchange and anisotropy parameters for the  $\text{FeF}_2$  system. The legend shown in the figure refers to the sets of exchange parameters for  $\text{FeF}_2$  called A, B(i), B(ii), B(iii), and C given by Hutchings *et al.* (see Table II). Experimental results for the Fe—Zn system are given as dark circles. For comparison, the corresponding experimental results (Ref. 1) (dark rectangles) and theoretical estimates (Ref. 4) (solid line) for the transition temperatures of the Mn—Zn system, are also included.

analysis we need not worry too much about this matter for as noted in Sec. II the  $\text{Fe}^{2+}$  ions feel about 10% larger anisotropy in  $\text{ZnF}_2$  than they do in  $\text{FeF}_2$ . Hence, as a first approximation, with increasing zinc content the reduction in  $D$  due to dipolar terms would almost exactly counterbalance the effective increase brought about by the zinc environment.

It should be stated that although such a detailed look at the nature of the present approximations and the use of a more complete self-consistency procedure would appear to move the computed results almost into coincidence with the experimental ones, we should like to refrain from getting too sanguine about it. The entire theoretical framework utilized here is itself subject to several percent uncertainty. Therefore, the present comments should only be taken to indicate that the simple self-consistency procedure used in this paper appears not to be unwarranted—at least, until more accurate experimental results become available and, equally importantly, a better understanding of how the exchange parameters themselves depend on the mixing has been achieved.

We might add here that our theory could also be extended to predict how the transverse susceptibility of the given system would depend on the zinc concentration and what its temperature dependence would be. Such additional experimental data would provide a very severe test of our parameter-free analysis. Indeed, it would even give us a feeling for whether the assumed independence of the exchange parameters on zinc concentration is fully justified or not. It is for this reason that we should like to make a plea to the experimentalists for: (a) more accurate  $T_C(x)$  results, (b) results

for transverse susceptibility on the same samples as a function of  $T/T_C(x)$ , and finally (c) for neutron-scattering data on such a mixed system.

## VI. CONCLUSIONS

The analysis presented in this paper leads us to two conclusions. First, we are able to shed light on the question raised by the experiments of Wertheim *et al.*<sup>1</sup>—this question is recorded in their closing paragraph where they say: “The reason for the difference of the behavior of  $\text{Fe}_x\text{Zn}_{1-x}\text{F}_2$  and  $\text{Mn}_x\text{Zn}_{1-x}\text{F}_2$  is not understood—” by concluding that it is the difference in the size and the nature of the anisotropy in the Fe-Zn and the Mn-Zn systems which is primarily responsible for the differences in their observed behavior. Secondly, we conclude that the simple CPA—RPA procedure—introduced in Refs. 3 and 10 and used earlier in Ref. 4—provides a convenient and useful tool for analyzing experimental data on mixed systems.

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