New effective-medium approach for randomly diluted uniaxial antiferromagnets: Application to $Fe_{1-x}Zn_xF_2$

F. G. Brady Moreira* and I. P. Fittipaldi
Departamento de Física, Universidade Federal de Pernambuco, 50.000 Recife, Pernambuco, Brasil
(Received 29 September 1980; revised manuscript received 10 April 1981)

A new model for uniaxial anisotropy in randomly diluted Heisenberg antiferromagnets, which is particularly appropriate for systems with high anisotropy, is presented. A generalized coherent-potential approximation has been developed to describe spin waves in those random systems where each spin is subjected to a local anisotropy field dependent on the magnetic (nonmagnetic) occupation of its neighborhood. The results are in very good agreement with recent experimental data for the antiferromagnetic resonance frequency in $Fe_{1-x}Zn_xF_2$.

Using inelastic light scattering technique, Montarroyos, de Araujo, and Rezende[1] have recently examined the behavior of the zero-field antiferromagnetic resonance (AFMR) frequency on the random system $Fe_{1-x}Zn_xF_2$, as a function of zinc concentration x. Their results showed a decrease in frequency with dilution (by nonmagnetic zinc) which is considerably less pronounced than the corresponding decrease on a related random system $Mn_{1-x}Zn_xF_2$ reported elsewhere.[2] The differences in the observed behavior of the AFMR frequency in these two systems certainly reveal the fundamental role played by the magnetic anisotropy. The weak anisotropy in manganese fluoride compounds is due to two-particle interactions, such as dipolar forces, while the relatively strong anisotropy in ferrous fluoride compounds in predominantly of crystal-field origin.

One of the most useful theoretical techniques for treating randomly diluted magnetic insulators have been based on the coherent-potential approximation (CPA). The CPA has been applied to these systems in several different ways.[3–7] However, all existing CPA formalism to date have neglected the effects of dilution on the single-ion crystal-field anisotropy. Indeed, most of these theories has been restrictly used to examine magnetic systems described by a Heisenberg exchange Hamiltonian in which the presence of a single-ion anisotropy is ignored. Moreover, as a general assumption, it is normally assumed that the only relevant parameters that enter in the description of diluted systems are those of the pure system. Although this might be possible in systems where the anisotropy is only of dipolar origin, and as such, has a simple linear dependence with dilution,[8] we expect that such a kind of description should not be suitable for those systems with crystal-field anisotropy.

In this article we propose a model for treating uniaxial anisotropy in randomly diluted magnetic insulators which allows us to describe the effects of dilution on both short- and long-range parts of the anisotropy. The long-range interactions are represented by a concentration-dependent anisotropy parameter, which is defined in terms of the effective anisotropy and exchange fields of the pure (undiluted) system. The other part is random in nature. Its randomness will be owed to occupation of the neighborhood of the magnetic site being considered. In order to describe such randomness we introduce a second parameter (here called local-anisotropy parameter) which is determined from the specification of the anisotropy fields in *both* extreme cases of $x=0$ and $x=1$. We believe that this feature, introduced by the present treatment, will be particularly important in studying properties related with small-$\vec{K}$ spin-wave modes of real disordered magnetic systems. Moreover, as has been pointed our by Dietrich *et al.*,[9] the effect of the differing environments in modifying the Ising energy of the different magnetic ions must be an essential aspect of a successful theory for treating these systems. It is therefore highly desirable to develop a general effective-medium approach applicable to a more general class of systems such as that which exhibits a random single-ion crystal-field anisotropy.

Accordingly we present in this paper a kind of CPA which takes into account the dynamical effects of fluctuations occasioned by both exchange and local anisotropy fields. In fact, the original motivation for this research was to seek a reliable theoretical method to estimate the effect of fluctuations in the crystal field on the basic properties of real diluted antiferromagnetic insulators, such as $Fe_{1-x}Zn_xF_2$.[10] As an application of this theory, we work out numerical calculations for the AFMR frequency using parameters appropriate to the (Fe-Zn) system and confront our results with the experimental data of Ref. 1.

We consider a spin model Hamiltonian described by

$$\mathcal{H}=2J\sum_{i,\delta}\sigma_i^{\lambda}\sigma_{i+\delta}^{-\lambda}\vec{S}_{i,\lambda}\cdot\vec{S}_{i+\delta,-\lambda}+\sum_{i,\lambda}\sigma_i^{\lambda}V_i^{\lambda}, \qquad (1)$$

where $\sigma_i^{\lambda}=1(0)$ if the site i is occupied (unoccupied) by a magnetic ion belonging to sublattice λ, and $-\lambda$ indicates the opposite interpenetrating sublattice to λ. $J>0$ is the exchange integral connecting nearest-neighbor pairs of spins, and V_i^{λ} is a single-ion anisotropy field given by

$$V_i^{\lambda}=-\bar{D}\left[1-\frac{\alpha}{z}\sum_{\delta}(1-\sigma_{i+\delta}^{-\lambda})\right](S_{i,\lambda}^{Z})^2. \tag{2}$$

Here we assume that V_i^{λ} will in general be dependent on the magnetic concentration through the concentration-dependent anisotropy parameter $\bar{D}$, and on the local environment of the site i (which consists of z neighbors) through the term involving the local anisotropy parameter α. Note that this model reduces to a previous one[8] in the case of $\alpha=0$, which corresponds to neglected local fluctuations in the anisotropy field. The Fourier transform of the configurationally averaged Green's function, $\Gamma_{\vec{K}}(E)$, at $T=0$, has the form

$$\Gamma_{\vec{K}}(E)=\begin{pmatrix}\Gamma_{\vec{K}}^{\uparrow,\uparrow}(E) & \Gamma_{\vec{K}}^{\uparrow,\downarrow}(E)\\ \Gamma_{\vec{K}}^{\downarrow,\uparrow}(E) & \Gamma_{\vec{K}}^{\downarrow,\downarrow}(E)\end{pmatrix}$$

$$=\frac{1}{F_{\vec{K}}(E)}\begin{pmatrix}E+2SzJ^{(E)}+(2S-1)[\bar{D}(1-\alpha)+D_{\downarrow}^{(E)}] & 2SzJ^{(E)}\\ -2SzJ^{(E)} & E-2SzJ^{(E)}-(2S-1)[\bar{D}(1-\alpha)+D_{\uparrow}^{(E)}]\end{pmatrix}, \tag{3}$$

$$F_{\vec{K}}(E)=\{E+2SzJ^{(E)}+(2S-1)[\bar{D}(1-\alpha)+D_{\downarrow}^{(E)}]\}\{E-2SzJ^{(E)}-(2S-1)[\bar{D}(1-\alpha)+D_{\uparrow}^{(E)}]\}+(2SzJ^{(E)}\gamma_{\vec{K}})^2 \tag{4}$$

with $\gamma_{\vec{K}}=z^{-1}\sum_{\delta}\exp(i\vec{K}\cdot\vec{\delta})$, where $\vec{\delta}$ denotes a nearest-neighbor vector. $D_{\uparrow}^{(E)}$, $D_{\downarrow}^{(E)}$, and $J^{(E)}$ are three parameters, which are introduced in order to define the effective coherent potential. For a given randomness and for each value of energy E, these CPA parameters are determined by requiring that the scattering from a pair of atoms immersed in a crystal described by such an effective medium shall be zero on average. This procedure leads to the following equations for determining $D_{\uparrow}^{(E)}$, $D_{\downarrow}^{(E)}$, and $J^{(E)}$.

$$\sum_{\sigma=0,1}\frac{P(\sigma)}{R(\sigma)}[V_J(\sigma)(\Gamma_{0,0}^{\downarrow,\uparrow}+\Gamma_{1,0}^{\downarrow,\uparrow})+V_D^{\uparrow}(\sigma)\Gamma_{0,0}^{\downarrow,\uparrow}+V(\sigma)\Gamma^{(2)}]=0, \tag{5a}$$

$$\sum_{\sigma=0,1}\frac{P(\sigma)}{R(\sigma)}[V_J(\sigma)(\Gamma_{0,0}^{\downarrow,\uparrow}+\Gamma_{1,0}^{\downarrow,\uparrow})+V_D^{\uparrow}(\sigma)\Gamma_{1,0}^{\downarrow,\uparrow}]=0, \tag{5b}$$

$$\sum_{\sigma=0,1}\frac{P(\sigma)}{R(\sigma)}[V_J(\sigma)(\Gamma_{1,1}^{\downarrow,\downarrow}+\Gamma_{0,1}^{\downarrow,\downarrow})+V_D^{\downarrow}(\sigma)\Gamma_{0,1}^{\downarrow,\downarrow}]=0, \tag{5c}$$

where $P(\sigma)$ takes the value $(1-x)$ for a connected bond, i.e., when $\sigma=1$, and the value x for and unconnected bond when $\sigma=0$. Here

$$R(\sigma)=1-V_J(\sigma)\Gamma^{(1)}-V_D^{\uparrow}(\sigma)\Gamma_{0,0}^{\downarrow,\uparrow}+V_D^{\downarrow}(\sigma)\Gamma_{1,1}^{\downarrow,\downarrow}-V(\sigma)\Gamma^{(2)},$$

$$V(\sigma)=[V_J(\sigma)+V_D^{\uparrow}(\sigma)][V_J(\sigma)+V_D^{\downarrow}(\sigma)]-[V_J(\sigma)]^2,$$

$$V_J(\sigma)=2S(J\sigma-J^{(E)}),$$

$$V_D^{\lambda}(\sigma)=(2S-1)(\alpha\bar{D}\sigma-D_{\lambda}^{(E)}),$$

$$\Gamma^{(1)}=\Gamma_{0,0}^{\downarrow,\uparrow}-\Gamma_{1,1}^{\downarrow,\downarrow}+2\Gamma_{1,0}^{\downarrow,\uparrow},$$

$$\Gamma^{(2)}=\Gamma_{0,0}^{\downarrow,\uparrow}\Gamma_{1,1}^{\downarrow,\downarrow}+(\Gamma_{1,0}^{\downarrow,\uparrow})^2,$$

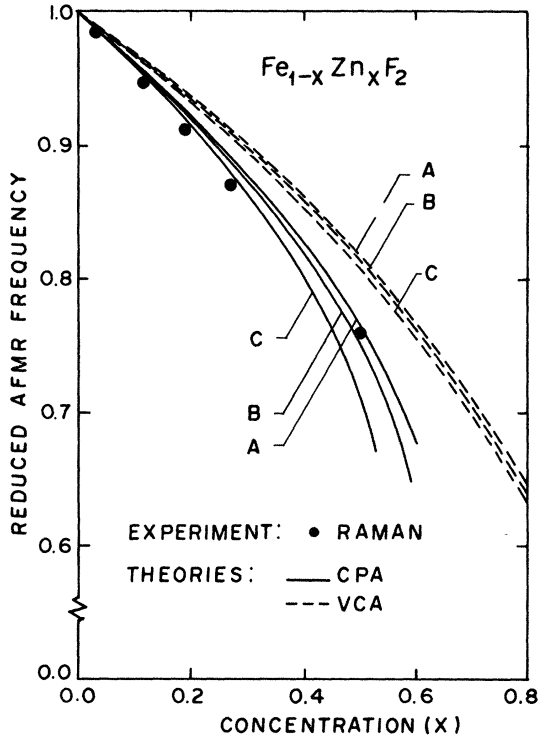

FIG. 1. Ratio, $E_0(x)/E_0(0)$, of AFMR frequency of the randomly diluted system $Fe_{1-x}Zn_xF_2$ and the pure system, FeF_2, as a function of the nonmagnetic concentration, x. Experimental results (•) correspond to the low-temperature (10 K) Raman data from Ref. 1. Theoretical estimates of the present work (continuous lines) marked A, B, and C were obtained with those values of parameters α and ρ listed in Table I. For comparison, the corresponding VCA estimates (dashed lines) are also included in the figure.

TABLE I. Parameters used to calculate the concentration dependence of the AFMR frequency in $Fe_{1-x}Zn_xF_2$. All the parameters are given in cm^{-1}.

CASE	$\bar{D}$	J	ρ	α
A	6.7	1.75	0.359	−0.239
B	6.72	1.839	0.342	−0.236
C	6.94	1.755	0.371	−0.196

and

$$\Gamma_{l,l'}^{\lambda,\lambda'} = N^{-1} \sum_{\vec{k}} \Gamma_{\vec{k}}^{\lambda,\lambda'} \exp[i(l-l')].$$

For calculating the AFMR frequency, $E_0(x)$, for a given nonmagnetic concentration, x, all that we need to know are the CPA parameters, $D_{\uparrow}^{(E_0)}$, $D_{\downarrow}^{(E_0)}$ and $J^{(E_0)}$, where E_0 is given by $F_{\vec{k}=0}(E_0)=0$. Within the present analysis, we have carried our numerical calculations appropriate to $Fe_{1-x}Zn_xF_2$ over a wide range of zinc concentrations. Typical results of the calculations are given in Fig. 1 where the reduced AFMR frequency $E_0(x)/E_0(0)$ is plotted as a function of zinc concentration for various values of the local anisotropy parameter α and the relative anisotropy parameter ρ, defined as $\rho=(2S-1)\bar{D}/2SzJ$. The relevant parameters are given in Table I. The different values of the exchange integral, J, and of the anisotropy parameter, $\bar{D}$, for the pure FeF_2 were obtained by fitting our dispersion relation (nearest-neighbor approximation in a bcc lattice) at the zone center with the experimental result of Ohlmann and Tinkham[11] ($E_0=52.7\ cm^{-1}$) and at the zone boundary (ZB) with several experimental results: of Fleury and Loudon[12] ($E_{ZB}=76.1\ cm^{-1}$; referred here as case *A*), Guggenheim *et al.*[13] ($E_{ZB}=79 cm^{-1}$; case *B*), and Hutchings *et al.*[14] ($E_{ZB}=77.1 cm^{-1}$; case *C*). On the other hand, the listed values for α were obtained by fitting (for each value of $\bar{D}$ in pure FeF_2) our anisotropy field [see Eq. (2)] in the extreme limit $H_A(x=1)=(2S-1)\bar{D}(1-\alpha)$, with the measured value $H_A(x=1)=24.9\ cm^{-1}$, on Fe^{2+} in ZnF_2, reported by Johnson and Sievers.[15] Further we notice that these values are found to be in reasonable agreement with the variation of the anisotropy field recently deduced experimentally.[16]

The calculations show a very good agreement between theory and experiment over a wide range of zinc concentrations; the differences are only about 6% (curve *C*) for $X=0.50$. In neither case has there been an attempt to include temperature dependence as well as instrumental resolution to the theoretical results. Part of the discrepancy may arise from such effects.

Calculations have also been made in the limit of virtual crystal approximation (VCA), for which $D_{\uparrow}^{(E)}=D_{\downarrow}^{(E)}=\rho\alpha z(1-x)$, and $J^{(E)}=J(1-x)$. In this limit, which is easily obtained from our CPA equations for large values of E and/or z, the resulting decrease in the AFMR frequency with dilution is observed to be less pronounced than the experimental one. Also, it should be noted that the VCA results are very much less sensitive to changes on α and ρ than those predicted by the present CPA formalism.

In summary, the analysis carried out in this paper leads us to conclude that only a kind of CPA formalism which takes into account dynamical effects of fluctuations occasioned by both exchange and anisotropy fields, would be able to describe systems with high anisotropy and for which the random nature of the anisotropy [given by Eq. (2)] plays a very important role. We also conclude that our approach is particularly appropriate for those systems and provides a convenient and reliable theoretical method for analyzing the experimental AFMR data on $Fe_{1-x}Zn_xF_2$.

The authors wish to thank E. Montarroyos, C. B. de Araujo, and S. M. Rezende for the communication of experimental results prior to publication. The many useful and enlightening discussions with Professor R. J. Elliott and Dr. R. B. Stinchcombe are also gratefully acknowledged. This work was partially supported by Conselho Nacional de Desenvolvimento Científico e Tecnológico and Financiadora de Estudos e Projetos (Brazilian Agencies).

*From November 1980 on leave of absence for two years at Department of Theoretical Physics, 1 Keble Road, Oxford, 0X1 3NP England.

[1]E. Montarroyos, C. B. de Araujo, and S. M. Rezende, J. Appl. Phys. 50, 2033 (1979); S. M. Rezende, C. B. de Araujo, and E. Montarroyos, J. Raman Spectrosc. 10, 173 (1981).

[2]A. R. King, S. M. Rezende, and V. Jaccarino, Bull. Am. Phys. Soc. 22, 332 (1977); M. C. K. Wiltshire, J. Phys. C 10, L37 (1977); W. E. Tennant and P. L. Richards, *ibid.* 10, L365 (1977).

[3]A. B. Harris, P. L. Leath, B. G. Nickel, and R. J. Elliott, J. Phys. C 7, 1693 (1974).

[4]W. J. L. Buyers, D. E. Pepper, and R. J. Elliott, J. Phs. C 6, 1933 (1973).

[5]R. A. Tahir-Kheli, Phys. Rev. B 6, 2808 (1972); A. Theumann and R. A. Tahir-Kheli, *ibid.* 12, 1796 (1975).

[6]R. A. Tahir-Kheli and A. R. McGurn, Phys. Rev. B 18, 503 (1978).

[7]L. M. Roth, J. Phys. C 12, 4879 (1979).

[8]F. G. Brady Moreira and I. P. Fittipaldi, J. Appl. Phys. 50, 1726 (1979).

[9]O. W. Dietrich, G. Meyer, R. A. Cowley, and G. Shirane, Phys. Rev. Lett. 35, 1735 (1975).

[10]It is worth mentioning that the CPA analysis described in Ref. 6 does ignore dynamical effects occasioned by fluctuations in the local anisotropy field and as such, within the scope of the type of analysis presented in Ref. 8, leads to unphysical results beyond certain critical concentration at which the theory breaks down.

[11]R. C. Ohlmann and M. Tinkham, Phys. Rev. 123, 425 (1961).

[12]P. A. Fleury and R. Loudon, Phys. Rev. 166, 514 (1968).

[13]H. J. Guggenheim, M. T. Hutchings, and B. D. Rainford, J. Appl. Phys. 39, 1120 (1968).

[14]M. T. Hutchings, B. D. Rainford, and H. J. Guggenheim, J. Phys. C 3, 307 (1970).

[15]K. C. Johnson and A. J. Sievers, Phys. Rev. B 10, 1027 (1974).

[16]C. B. de Araujo, Phys. Rev. B 22, 266 (1980).