On the Magnetic Susceptibility of Interacting Spin-pair Systems

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Modifying a general theory of antiferromagnetism proposed by Oguchi, the parallel and perpendicular magnetic susceptibilities ($\chi_{//}$ and $\chi_{\perp}$ respectively) of antiferromagnetically interacting spin-pair systems have been formulated. As the parameter of the equations, $\kappa=z|J'|/|J|$, approaches zero, both of them coincide with a familiar equation of isolated spin-pairs. In the $0<\kappa\leq1$ range the maximum susceptibility and the Weiss constant are compared with those estimated exactly by the alternating antiferromagnetic linear-chain model. For $1<\kappa\leq2$, they can be characterized by a broad maximum and a transition to the antiferromagnetically ordered state. For $\kappa>2$, $\chi_{//}$ and $\chi_{\perp}$ show curves similar to those of a typical three-dimensional antiferromagnet. The $\chi_{//a}$ and $\chi_{\perp a}$ of the 2,2-diphenyl-1-picrylhydrazyl–benzene (1: 1) complex have been examined based on the theoretical results for $\kappa=1.3$. The magnetic susceptibilities of the other organic free radicals have been compared with the results calculated in the $0\leq\kappa<1$ range.

Since the first observation of two-spin clusters in $Cu(CH_3COO)_2$ by means of electron paramagnetic resonance (EPR) and magnetic susceptibility (χ) measurements, many examples of such spin-pair systems in organic and inorganic materials have been studied by a number of investigators.[1] The χ or the EPR intensity has usually been characterized by a familiar equation:

$$\chi = \frac{N(g\mu)^2S(S+1)}{2kT[3+\exp(2|J|/kT)]} \tag{1}$$

where J is the interaction between two spins coupled antiferromagnetically; μ, the Bohr magneton, and g, the Lande g-factor, and where the other notations have the usual meanings. This equation, however, cannot be applied to systems with comparatively large inter-pair interactions. In 1955 Oguchi[2] developed a general theory of ferromagnetism and antiferromagnetism, based on the Heisenberg model of two-spin clusters. Modifying this theory, one can calculate analytically and tractably the susceptibility of interacting spin-pair systems. In this paper this theory will be extended to antiferromagnetically interacting spin-pair systems in order to understand qualitatively their physical behavior by relatively simple formulations. Based on the theoretical results thus derived, first we will examine the magnetic susceptibility of 2,2-diphenyl-1-picrylhydrazyl–benzene (1: 1) complex (DPPH–Bz) measured by Fujito.[3] Recently it was shown for the complex that none of the isolated spin-pair, linear chain, or quadratic net Heisenberg models give a satisfactory agreement with the experimental results.[4] The main object of applying our model to DPPH–Bz, therefore, is to examine its magnetic property in relation to spin-cluster models. Secondly, the χ values of some organic free radicals with small or intermediate inter-pair interactions are compared with the theoretical results obtained by our model and the alternating linear-chain model developed by Duffy and Barr.[5]

Theoretical

We treat here a spin-pair, whose spin operators are denoted by $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$, interacting with each other with a negative exchange interaction $-|J|$. For the sake of simplicity, it is assumed hereafter that g is isotropic and S is 1/2. Such assumptions can reasonably be accepted in spin systems consisting of usual organic free radicals. In addition to J inter-pair exchange interaction, $J'(|J'|<|J|)$, is introduced in the system. Then, the Hamiltonian can be written as

$$\mathcal{H} = 2|J|(\boldsymbol{S}_i\cdot\boldsymbol{S}_j) + 2|J'|[\sum_k(\boldsymbol{S}_i\cdot\boldsymbol{S}_k)+\sum_l(\boldsymbol{S}_j\cdot\boldsymbol{S}_l)] + g\mu H^z(S_i^z+S_j^z), \tag{2}$$

where the sums k and l go over the nearest neighbors of the i-spin except for the j-spin, and of the j-spin except for the i-spin, respectively. Here, the last term is the Zeeman energy of the system with an external magnetic field, H^z, along the easy axis, hereafter denoted as the z-axis. According to the usual molecular field approximation, $\boldsymbol{S}_k$ and $\boldsymbol{S}_l$ are replaced by their thermal mean expectation values, $-\bar{S}$ and $+\bar{S}$, respectively, which change to $\mp\bar{S}+\delta\bar{S}^z$ by the application of the magnetic field along the z-axis. Thus, the Hamiltonian can simply be written as

$$\mathcal{H} = 2|J|(\boldsymbol{S}_i\cdot\boldsymbol{S}_j) + aS_i^z + bS_j^z, \tag{3}$$

where

$$a = 2|J'|z(-\bar{S}+\delta S^z) - g\mu H^z,$$
$$b = 2|J'|z(+\bar{S}+\delta S^z) - g\mu H^z, \tag{4}$$

and where z is the number of the nearest neighbors of the i-spin, excluding the j-spin. Next, we define a new parameter, $\kappa=z|J'|/|J|$, which means the strength of the molecular field. For simplicity in the description, we adopt the exchange interaction, $|J|$, as the unit of the energy. Then,

$$\mathcal{H} = 2(\boldsymbol{S}_i\cdot\boldsymbol{S}_j) + [2\kappa(-\bar{S}+\delta S^z)-h]S_i^z + [2\kappa(\bar{S}+\delta S^z)-h]S_j^z, \tag{3'}$$

where $h=g\mu H/|J|$. Using the spin states $\alpha_i\alpha_j$, $(1/\sqrt{2})(\alpha_i\beta_j+\beta_i\alpha_j)$, $\beta_i\beta_j$ and $(1/\sqrt{2})(\alpha_i\beta_j-\beta_i\alpha_j)$, the eigen values of Eq. 3′ are derived as

$$E_1 = (1+4\kappa\delta S^z-2h)/2,$$
$$E_2 = (-1/2) + R,$$
$$E_3 = (1-4\kappa\delta S^z+2h)/2,$$
$$E_4 = (-1/2) - R, \tag{5}$$

where

$$R = (1+4\kappa^2\bar{S}^2)^{1/2}. \tag{6}$$

Now the magnetization in the external magnetic field along z-axis is defined self-consistently as

$$\bar{S} + \delta S^z = \mathrm{Tr}\, S^z e^{-\beta\mathcal{H}} / \mathrm{Tr}\, e^{-\beta\mathcal{H}} \tag{7}$$

where $\beta = 1/t = |J|/kT$. By substituting Eq. 5 into Eq. 7, we obtain

$$\bar{S} + \delta S^z = \frac{1}{2} \cdot \frac{\frac{2\kappa}{R}\bar{S}e^{\beta}\sinh\beta R + \sinh(h - 2\kappa\delta S^z)}{\cosh(h - 2\kappa\delta S^z) + e^{\beta}\cosh\beta R}. \tag{8}$$

As the terms containing h and S^z are small quantities of the first order, one can divide Eq. 8 into two parts. The zeroth-order term is

$$\bar{S} = \frac{\kappa\bar{S}\sinh\beta R}{R(e^{-\beta} + \cosh\beta R)} \tag{9}$$

which leads to the non-zero solution of $\bar{S}$. At the limit of $R=1$, the Néel temperature, $T_N = |J|/k\beta_N$, can be calculated from:

$$e^{-\beta_N} + \cosh\beta_N = \kappa \sinh\beta_N \tag{10}$$

As a function of κ, the solution of this equation is shown in Fig. 1. The lower part of the solid line of the figure is the antiferromagnetically ordered state, denoted as AF, while its upper part is the paramagnetic region (P). It should be noted here that in the $0 \leq \kappa < 1$ range no antiferromagnetic transition occurs.[6]

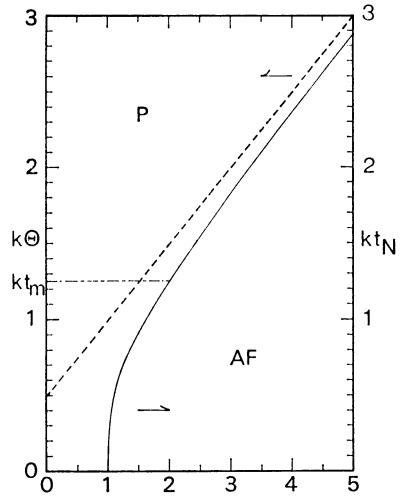

Fig. 1. The reduced Néel temperature (t_N: solid line), Weiss temperature (Θ: broken line), and temperature showing broad maximum of the susceptibility (t_m: dotted broken line) *versus* the molecular field parameter κ. AF: Antiferromagnetic state, P: Paramagnetic state.

From the first-order term of Eq. 8:

$$\chi_{\parallel} = Ng\mu\left(\frac{\delta S^z}{\delta H}\right)_{H=0} = \frac{1}{2}\,\frac{N(g\mu)^2\beta}{\kappa\beta + 1 + e^{\beta}\cosh\beta R}. \tag{11}$$

By a manner similar to that used with $\chi_{//}$, the magnetic susceptibility perpendicular to the z-axis ($\chi_{\perp}$) is given as:

$$\chi_{\perp} = \frac{(R-1)^2 e^{\beta}\cosh\beta R + 2R - (R^2+1)e^{\beta(1-R)}}{\{2\kappa[(R-1)^2 e^{\beta}\cosh\beta R + 2R(R^2+1)e^{\beta(1-R)}] + 2R(R^2-1)(1+e^{\beta}\cosh\beta R)\}}. \tag{12}$$

In the paramagnetic region ($\bar{S}=0$), Eq. 12 coincides with Eq. 11 if we take the limit of $R = 1+\delta$ as δ approaches 0. Furthermore, for $\kappa = 0$ Eqs. 11 and 12 coincide with Eq. 1 for $S = 1/2$. In Fig. 2 the powder susceptibilities $\chi = (\chi_{//} + 2\chi_{\perp})/3$, are shown as functions of the reduced temperature, t. The numbers in the figure are the values of κ.

We will now show some typical cases of Eqs. 11 and 12. At high temperatures ($t \gg 1/k$), χ becomes a simple form:

$$\chi = \frac{N(g\mu)^2}{4k} \cdot \frac{1}{t - (-\Theta)}, \tag{13}$$

where $\Theta (= (\kappa+1)/2k)$ is called the Weiss temperature. The dependence of Θ on κ is also shown in Fig. 1 by a broken line which coincides with the asymptote of the solid line.

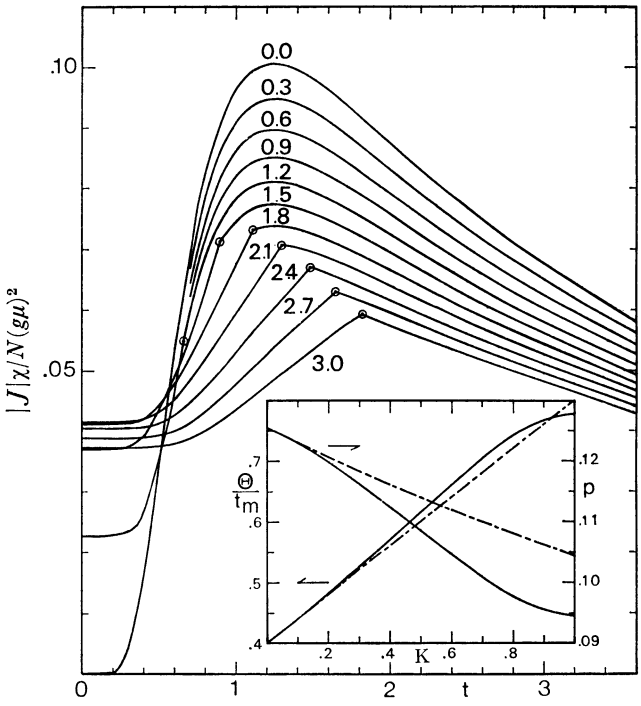

Fig. 2. The powder magnetic susceptibility *versus* the reduced temperature for $\kappa = 0.0$ to 3.0. The Néel temperatures are indicated by the circles in the figure. The inset shows the Weiss temperature divided by t_m and the product of maximum susceptibility times t_m, $p = \chi_m k t_m / Ng^2\mu^2$, *versus* the molecular field parameter κ (broken line) compared with the alternating linear chain model (solid line) (Ref. 5).

At moderate temperatures comparable to $|J|/k$, χ depends sensitively on κ. For $0 \leq \kappa < 1$, Θ shows a broad maximum at a constant temperature, $t_m (= 1.2473/k)$, without any phase transition. The inset in Fig. 2 shows the variations in the dimensionless Θ/t_m and of

$$p = \chi_m k t_m / N(g\mu)^2 \tag{14}$$

as functions of κ. In this range of κ for $z=1$, our results can be compared with the magnetic susceptibility of the alternating linear chain calculated exactly by Duffy and Barr.[5] Also shown by the solid line in the inset of Fig. 2 are the results of their theoretical calculations. Θ/t_m is in good agreement with their value, while p deviates upward as κ increases, the deviation being

about 10% at $\kappa=1$. For $\kappa<0.3$, however, our susceptibility calculations agree well with those by Duffy and Barr with the deviation of only 2%. The deviation of p for κ values larger than 0.3 in the inset is mainly due to the energy separation between the singlet ground state and the excited triplet states (Δ). In our model, Δ can be derived from Eq. 5 for $h=0$ and $R=1$ as $\Delta=2$ in units of $|J|$. This constant value of Δ in the paramagnetic state is one of the features of our simple model. For a more quantitative analysis of χ, it is desirable that Δ be explicitly expressed as a function of J' or κ, as will be discussed later. In the case of the alternating linear-chain model, on the other hand, Δ for $h=0$ depends on the continuous-energy spectrum, which is expressed as $\Delta(k)=2-\kappa\cos k$.[5]

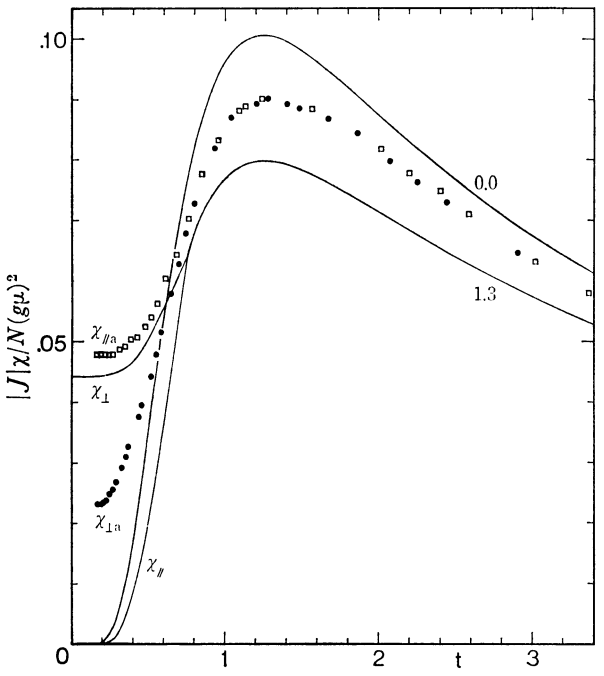

Fig. 3. The magnetic susceptibilities of the DPPH–Bz complex along a-axis (square) and perpendicular to a-axis (full circle) *versus* the reduced temperature t for $|J|/k=0.54$ K. Solid lines are the theoretical calculations by Eqs. 11 and 12 for $\kappa=0.0$ and 1.3.

In the antiferromagnetic region ($t>t_N$, $R>1$) $\chi_{//}$ decreases rapidly with a decrease in the temperature, while $\chi_{\perp}$ gives a constant value near absolute zero. Its magnitude depends approximately on κ as follows:

$$\chi_{\perp}(0) \fallingdotseq (\kappa-1)/4\kappa^2 \qquad (15)$$

As an illustrative example, the calculated $\chi_{//}$ and $\chi_{\perp}$ values for $\kappa=1.3$ are shown in Fig. 3 as functions of t. Such special susceptibilities can be experimentally visualized by a stable free radical, DPPH–Bz, as will be shown in the following section. In the antiferromagnetic region, Eq. 5 explicitly includes J', even for $h=0$. Therefore, our model is considered to be a good approximation compared with the case in the paramagnetic region mentioned above.

By a comparison of Eqs. 11 and 12 with the experimental results, one can estimate J' in addition to J, provided that z can be derived crystallographically. It should be noted, however, that the estimated J' is fundamentally not the real value, because, in the approximation treated here, we use a mean value of the molecular field produced by the neighbors.

Comparison with Experiments

Magnetic Susceptibility of DPPH–Bz Single Crystal. We will examine here the magnetic susceptibilities along the a-axis and perpendicular to the a-axis of the DPPH–Bz complex, hereafter denoted as $\chi_{//a}$ and $\chi_{\perp a}$ respectively.[3] In a previous paper[7] the powder susceptibility of DPPH–Bz at temperatures lower than 1.7 K, which were measured by a bridge method in a zero static field, were fitted to the value at 1.7 K measured by a force method in the field of 0.829 T. By this procedure, however, the values below 1.7 K were overestimated, because the $\chi_{//}$(also $\chi_{\perp}$) values of spin-pair systems with a singlet ground state depends on the applied magnetic field. In the paramagnetic region ($R=0$), for example, one can simply derive the χ as a function of the external field from Eq. 8 as

$$\frac{|J|\chi(t,h')}{N(g\mu)^2} = \frac{\beta/2}{1+\kappa\beta+e^{\beta}\cosh\beta/\cosh\beta h'} \qquad (16)$$

where $h'=h-2\kappa\delta S^z$ is the effective field including the contribution from the induced magnetization. At temperatures higher than $|J|/k$, this contribution can be neglected ($h'=h$). $|J|/k$ was estimated to be 0.54 ± 0.02 K from the temperature (T_m) at which χ reached χ_m. By substituting this value into Eq. 16, the χ of DPPH–Bz at 1.7 K in 0.829 T is estimated to be 10% larger than that in the zero field. The experimental data in Fig. 3, measured by the bridge method were, therefore, calibrated by the value measured by the force method at 4.22 K which was corrected using Eq. 16. The anisotropy of the susceptibility ($\chi_{//a}-\chi_{\perp a}$) appeared at around 0.42 K at which the low-field EPR absorption line disappeared.[3] This behavior coincided with that which occurs around the Néel temperature of antiferromagnetic materials.[8] Therefore, we tentatively adopted 0.42 K as the T_N of DPPH–Bz. The ratio of T_m to T_N, 1.62, was used to determine the value of κ. The theoretical susceptibilities calculated for $|J|/k=0.54$ K and $\kappa=1.3$ are compared with $\chi_{\perp a}$ and $\chi_{//a}$ in Fig. 3. $\chi_{\perp}$ reproduces well the temperature dependence of $\chi_{//a}$. $\chi_{\perp a}$ also shows a value similar to $\chi_{//a}$ at t near t_N, but approaches a finite value as the temperature decreases. This is probably due to the lack of coincidence of the observed axis with the easy axis of the crystal.

Above t_N, on the other hand, the experimental values in Fig. 3 are just in the middle between those for $\kappa=0$ and 1.3. Such a deviation from our theoretical calculations for $\kappa=1.3$ in the paramagnetic region may indicate: 1) a cooperative phenomenon caused by J' and similar to those in the magnetic linear-chain and quadratic net Heisenberg models, or 2) the energy splittings of the degenerate triplet states by J', even in the range of the paramagnetic state. Recently Duffy, Strandburg and Deck[4] reported the susceptibility and

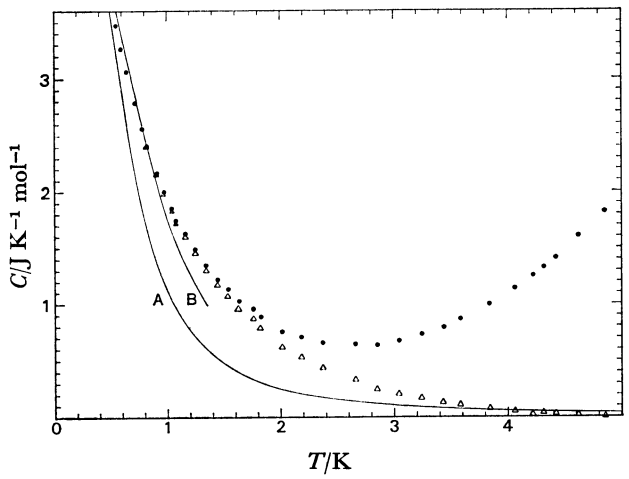

Fig. 4. Comparison of theoretical calculations of heat capacity with experimental data of DPPH–Bz measured by Duffy *et al.* (Ref. 4). A: Eq. 17, B: Two-spin-pair model calculated by Duffy and Barr (Ref. 5), ●: total heat capacity, △ magnetic part of the heat capacity.

the heat capacity (C_v) of DPPH–Bz from 0.4 K to room temperature, with which neither the linear-chain nor the quadratic net Heisenberg model gives satisfactory agreement. Therefore, the latter possibility described above may contribute to the deviation from the theoretical values.

Their heat-capacity data, shown in Fig. 4, are helpful in understanding the magnetic interactions of DPPH–Bz. Using Eq. 5, C_v of our model can be derived as

$$C_v = 6kN\beta^2|J|^2/(3e^{-\beta|J|}+e^{\beta|J|})^2 \qquad (17)$$

which coincides with the C_v of the isolated spin-pair systems, because in the paramagnetic state the energy levels under consideration are equal to those of the isolated spin-pair systems. A in Fig. 4 is calculated by means of Eq. 17 for $|J|=0.54\,k$. As has already been pointed out for the susceptibility data, the experimental data of C_v also deviate upward from A. For the linear-chain model, the magnitude of the theoretical heat capacity and the $\chi_m T_m$ values are quite low.[4] One of the possible ways to interpret both the susceptibility and heat capacity is to include J' in Eq. 5 explicitly, even in the paramagnetic region. Dufly and Barr[5] calculated the C_v of an alternative four-membered ring with $J'=0.8\,J$, a kind of two-spin-pair model, which is also shown in Fig. 4 as B for the sake of comparison. The agreement of B with the experimental results is better than that of A. The two-spin-pair model, therefore, is an improvement of the model for DPPH–Bz. Thus, one can conclude that our simple model well explains the appearance of t_N in addition to the temperature dependence of the magnetic susceptibilities of DPPH–Bz if we adopt 0.42 K as the T_N of DPPH–Bz. For the quantitative agreement of the susceptibilities, however, it is desirable to take into account the energy splittings in the triplet states. Some formulations according to such a modification are now in progress.

Table 1. Molecular-field parameter, κ, estimated from the maximum susceptibility of some organic free radicals

Compound	$\frac{T_m}{K}$	$\frac{\lvert J\rvert}{K}$	$\chi_m \times 10^4$ g)	$\frac{\lvert J\rvert\chi_m}{N(g\mu)^2}$	κ
Sulfite[a)]	15	12	127	0.101	0.02
DPPH-free[b)]	11	8.8	170	0.10	0.05
DPPH-free[c)]	10.5	8.75	177	0.099	0.06
TEMPAD[d)]	16.5	13.2	100	0.089	0.72
Porphyrexide[e)]	7.2	5.8	228	0.088	0.73
PAC[f)]	70	55	23.3	0.087	0.77
$D(NO_2)_2$[f)]	9.7	7.8	167	0.0863	0.82

a) A. Nakajima, H. Ohya-Nishiguchi, and Y. Deguchi, *Bull. Chem. Soc. Jpn.*, **45**, 713 (1972). b) Ref. 6. c) P. Grobet, L. Van Gerven, and A. Van den Bosch, *J. Chem. Phys.*, **68**, 5225 (1978). d) A. Nakajima, H. Nishiguchi, and Y. Deguchi, *J. Phys. Soc. Jpn.*, **24**, 1175 (1968). e) T. Fujito, H. Nishiguchi, Y. Deguchi, and J. Yamauchi, *Bull. Chem. Soc. Jpn.*, **42**, 3334 (1969). f) W. Duffy and D.L. Strandburg, *J. Chem. Phys.* **46**, 456 (1967). g) Corrected for the magnetic "impurities" as required.

Examples of Other Organic Free Radicals. In order to show the applicability of our model, the χ values of other compounds are compared with those calculated by means of Eq. 11. Table 1 summarizes the compounds with the values of $\kappa<1$. We can also derive the values of the parameter from Θ, but this method is not so reliable because of the large experimental errors. The $|J|$ values were estimated from T_m. It has been concluded that the sulfite and the DPPH-free are mostly isolated spin-pairs, while the others have comparatively large inter-pair interactions. For comparison with the experimental results on 2,2-bis(*p*-nitrophenyl)-1-picrylhydrazyl ($D(NO_2)_2$), Duffy and Barr estimated the alternation parameter (a) of the alternating linear-chain model as $a=0.6$, which corresponds to our value of $\kappa=0.9$ in the inset of Fig. 2. Thus, the molecular-field approximation of interacting spin-pair systems is useful for a physical understanding of complicated organic free radicals.

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3) T. Fujito, *Bull. Chem. Soc. Jpn.*, to be published.
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5) W. Duffy, Jr., and K. P. Barr, *Phys. Rev.*, **165**, 647 (1968).
6) In the $0<\kappa<1$ range Yamashita and Amaya discussed the thermodynamical properties of the interacting spin-pair systems, including the perpendicular part of the molecular field, and pointed out another type of spin ordering. See N. Yamashita and K. Amaya, *J. Phys. Soc. Jpn.*, **41**, 419 (1976), and other references cited therein.
7) T. Fujito, T. Enoki, H. Ohya-Nishiguchi, and Y. Deguchi, *Chem. Lett.*, **1972**, 557.
8) See, for example, S. Foner, "Magnetism I," ed by G. T. Rado and H. Suhl, Academic Press, NY (1963), p. 383.