

Local and Nonlocal Magnetization of Impurities in Linear Antiferromagnetic Chains

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An Ising model with ferromagnetically coupled, randomly distributed impurities in a linear antiferromagnetic chain was previously presented to interpret the magnetization of certain organic free radicals. Simple assumptions permit this model to be generalized to other anisotropies. It is shown that for a small concentration of impurities there are two contributions to the low-temperature magnetization. One is a local contribution and is proportional to the number of impurities, q . It is largest and least localized for Heisenberg coupling. The other contribution is nonlocal, depends upon the zero-temperature long-range order ω_∞ , and probably can be represented as a single spin of magnitude $g\beta(\omega_\infty q)^{1/2}/2$. Near the Ising limit the system acts like a superparamagnet. The magnetic-field dependence of the magnetization can be used to separate the two contributions. For Heisenberg coupling the magnetization will be paramagnetic and this paramagnetism persists as $kT/|J| \rightarrow 0$. This prediction requires $\omega_\infty = 0$ and hence provides a direct test of this relation. The low-temperature experimental results on the free radicals agree with the paramagnetism predicted in the case of Heisenberg coupling.

I. INTRODUCTION

THERE has been considerable progress recently in determining the properties of linear antiferromagnetic chains.¹⁻⁶ Unfortunately, measurements of such thermodynamic quantities as the susceptibility, magnetization, specific heat, etc., do not provide very complete information about the ordering. In this paper the low-temperature magnetization of an antiferromagnetic chain containing a low concentration of ferromagnetically coupled impurities will be investigated. It will be shown how these impurities can be used as probes to provide information about the ordering. In particular, they allow an experimental test of whether the zero-temperature long-range order ω_∞ is zero for Heisenberg coupling.

In Ref. 7 the model is presented and some of its predictions compared with experimental results on certain organic free radicals. Some organic free radicals represent linear antiferromagnetic chains in which the low-temperature susceptibility is dominated by impurities.⁷ The impurities appear to be coupled via exchange forces to their neighbors, and yet still give rise to a paramagnetic contribution to the susceptibility. In order to interpret these data, an Ising model containing ferromagnetically coupled impurities was introduced. Falk⁸ has generalized this model for other values of spin, but his work has the same limitations with regard to temperature range or impurity concentration. These limitations can be partially removed by the method of Ref. 9. In Ref. 9 it was shown that the low-temperature limit of the model results in superparamagnetism. No superparamagnetism is indicated in the

experimental results on the free radicals. Because of this and the fact that the interaction between the spins in the free radicals is better represented by Heisenberg coupling, it is interesting to try to generalize this model to other anisotropies. For Heisenberg coupling the zero-temperature long-range order ω_∞ is probably zero. In Ref. 9 it was suggested that in the case of Heisenberg coupling, the impurities would act paramagnetically. This suggestion was based on an analogy to the result for a gas of impurities for which the effective ω_∞ is zero. This suggestion will be proved using simple approximations. A system in which the anisotropy can vary between the Heisenberg and Ising limits is investigated. The restriction to Ising coupling will be removed by making some approximations which should be qualitatively correct. The approximations become exact in the case of Ising coupling, but their correctness is difficult to test for other anisotropies. They are simple and rather natural approximations in the sense that they are reasonable and the first ones to come to mind.

The treatment is restricted to low temperatures, low impurity concentrations, and finite-size systems. The last restriction is not necessary in the case of Heisenberg coupling and for some of the results when the coupling is intermediate between Heisenberg and Ising coupling. Use is made of the zero-temperature correlations. The magnetization is developed as a power series in $g\beta H/kT$. It is necessary to evaluate at least two terms in this series in order to separate the paramagnetic and nonparamagnetic contributions to the magnetization. It will be shown that in general the impurity gives rise to two effects. There is a contribution to the magnetization which is localized near the impurity site. The magnitude and extent of this local contribution, but not its existence, depend upon the approximations which are made. It is interesting to note that Tonegawa and Kanamori¹⁰ have found a localized mode in their spin-wave analysis of the three dimensional case. From the approximations it follows that the local moment

¹⁰ T. Tonegawa and J. Kanamori, Phys. Letters **21**, 130 (1966).

¹ J. C. Bonner and M. E. Fisher, Phys. Rev. **135**, A640 (1964).

² R. B. Griffiths, Phys. Rev. **133**, A768 (1964).

³ Z. G. Soos, J. Chem. Phys. **43**, 1121 (1965).

⁴ A. S. Edelstein, Phys. Rev. **142**, 259 (1966).

⁵ K. Kawasaki, Phys. Rev. **142**, 164 (1966).

⁶ K. Kawasaki, Ann. Phys. (N.Y.) **37**, 142 (1966).

⁷ A. S. Edelstein, J. Chem. Phys. **40**, 488 (1964).

⁸ H. Falk, Phys. Rev. **151**, 304 (1966).

⁹ A. S. Edelstein, J. Chem. Phys. **42**, 2879 (1965).

can be expressed as a sum of the partial sums S_n which were defined in Ref. 4. There it was shown that the S_n 's provide bounds on the product of the temperature times the susceptibility.

Besides the local contribution, there is a superparamagnetic contribution. This is a result of the large distance correlations approximating ω_∞ . The superparamagnetic effect vanishes if the zero-temperature long-range pair correlation ω_∞ is zero. In this case, thought to occur for Heisenberg coupling, the local contribution remains and behaves paramagnetically as $kT/|J| \rightarrow 0$. This example of paramagnetic behavior in a strongly coupled exchange system is interesting and perhaps unique.

II. THE MODEL AND LOWEST-ORDER TERM IN H

A. Formalism

The Hamiltonian under consideration is

$$\mathcal{H} = \mathcal{H}_E + \mathcal{H}_z, \quad (1)$$

$$\mathcal{H}_z = -g\beta \sum_{i=1}^N S_i^z H, \quad (2)$$

$$\mathcal{H}_E = -2 \sum_{i=1}^N J_{i,i+1} [S_i^z S_{i+1}^z + \gamma (S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)], \quad (3)$$

where

$$\begin{aligned} J_{i,i+1} &= J' > 0 && \text{if } i \text{ and } i+1 \text{ are both impurity} \\ & && \text{neighbors} \\ &= J < 0 && \text{otherwise,} \end{aligned} \quad (4)$$

and the magnetic field is in the z direction. All the spins have $S = \frac{1}{2}$. The impurities are nonmagnetic and are responsible for a ferromagnetic superexchange between their nearest neighbors. They were previously called diamagnetic impurities.^{7,9} The number of impurities will be denoted by q and they will be assumed to be randomly distributed. The total number of pure spins is denoted by N . (This is a slight change from the previous notation.) The spins are arranged in a ring and hence cyclic boundary conditions will be employed; i.e., $S_{N+1} \equiv S_1$.

The magnetization is

$$M = g\beta \text{Tr} \left[\sum_{i=1}^N S_i^z \exp(-\mathcal{H}/kT) \right] / \text{Tr} \left[\exp(-\mathcal{H}/kT) \right], \quad (5)$$

$$\begin{aligned} \frac{4kTM}{(g\beta)^2 H} &= \langle \sum_{ij} \sigma_i \sigma_j \rangle + \frac{1}{2} \left(\frac{g\beta H}{2kT} \right)^2 \left[\frac{1}{3} \langle \sum_{ijkl} \sigma_i \sigma_j \sigma_k \sigma_l \rangle \right. \\ &\quad \left. - \langle \sum_{ij} \sigma_i \sigma_j \rangle^2 \right] + \text{terms of order} \left(\frac{g\beta H}{2kT} \right)^4, \end{aligned} \quad (6)$$

where for any operator O

$$\langle O \rangle \equiv \text{Tr} [O \exp(-\mathcal{H}_E/kT)] / \text{Tr} [\exp(-\mathcal{H}_E/kT)], \quad (7)$$

$$\sigma_i = 2S_i^z. \quad (8)$$

B. Approximations

Consider the first term on the right of Eq. (6). At present this term can only be calculated if $\gamma = 0$; i.e., for Ising coupling.⁹ It can be evaluated in the limit of very low temperatures⁴ for any γ in the absence of impurities. In order to proceed further it is necessary to make some approximations, the validity of which is difficult to ascertain. As mentioned earlier, the approximations are reasonable and the first ones that come to mind. It is assumed that the low-temperature correlation between spins i and j is unmodified by the impurities if there are no intervening impurities between the spins i and j ; i.e.,

$$\langle \sigma_i \sigma_j \rangle \approx \langle \sigma_i \sigma_j \rangle_{\text{pure}}. \quad (9)$$

If there are intervening impurities it is assumed that

$$\langle \sigma_i \sigma_j \rangle \cong (-1)^m \langle \sigma_i \sigma_j \rangle_{\text{pure}}, \quad (10)$$

where m is the number of intervening impurities and $\langle \sigma_i \sigma_j \rangle_{\text{pure}}$ is the correlation between spins i and j in a chain without impurities. This assumption is correct for Ising coupling, $\gamma = 0$, if $J' = -J$. One can consider taking the J'/J ratio which best satisfies Eq. (10). For $\gamma \neq 0$, there may not be any value for this ratio which satisfies Eq. (10). Nevertheless, the predictions based on this equation should be qualitatively correct. The factor $(-1)^m$ correctly describes the effect of ferromagnetic coupling on whether spins tend to be parallel or antiparallel.

By restricting the treatment to low temperatures one is able to obtain numerical values for some of the first terms in the Taylor series expansion of the magnetization. Following the approach used in Ref. 4, it is reasonable to take

$$\begin{aligned} \langle \sigma_i \sigma_j \rangle_{\text{pure}} &\approx \omega_{j-i}, && \text{for } kT \ll |J| \\ & && \text{and } |j-i| \lesssim 1000. \end{aligned} \quad (11)$$

The ω 's are the zero-temperature correlations between spins in the absence of impurities. See Ref. 1 for the values of ω_l and Ref. 4 for a general discussion of the ordering in the pure-spin case. For $kT \ll |J|$, short-range ordering extends over a certain range taken in Eq. (11) to be 1000 spins. Within this range the finite temperature correlations are approximately equal to their zero-temperature values. For decreasing temperature the range of validity of Eq. (11) and accuracy of the approximation are expected to increase. It will be useful to employ Eq. (11) throughout. This implies that some of the results are valid only for finite size systems. These instances will be pointed out. Combining

Eqs. (10) and (11) one has

$$\langle \sigma_i \sigma_j \rangle \approx (-1)^m \omega_{j-i}, \quad \text{for } kT \ll |J| \\ |j-i| \lesssim 1000. \quad (12)$$

The problem can be simplified by taking the concentration c of impurities to be small. Hence the average impurity separation is large. This will allow the correlation between spins near different impurities on an average to be approximately equal to $\pm\omega_\infty$, where

$$\omega_\infty \equiv \lim_{|i-j| \rightarrow \infty} |\langle \sigma_i \sigma_j \rangle| = \lim_{l \rightarrow \infty} |\omega_l|. \quad (13)$$

There will always be some impurities which will be close to one another, but for decreasing c , the percentage within any separation ξ decreases. As discussed in Ref. 4, the correlations $|\omega_l|$ decrease with increasing l and for some separation $\xi(\epsilon)$, $|\omega_l| - \omega_\infty| < \epsilon$ for all $l \geq \xi$. Because the ω 's are of order unity a reasonable choice of ϵ is 0.01. The values of $\xi(0.01)$ can be estimated from Bonner and Fisher's values of ω_l .

The necessary value of ξ is maximum for Heisenberg coupling $\gamma=1$ and decreases rapidly to 1 at $\gamma=0$. For $\gamma=1$, ξ is difficult to estimate because the ω 's have only been calculated out to ω_4 and the rate of decrease is slow.

The probability that the two impurities are separated by n spins is $c(1-c)^n$. This follows from the assumed randomness of the impurities; i.e., the probability that any site is occupied by an impurity is c . The requirement that most of the impurities are separated by $\xi-1$ or more spins is that the sum of the probabilities of smaller separations is small, or

$$c \sum_{m=0}^{\xi-1} (1-c)^m \ll 1. \quad (14)$$

This implies

$$c \ll 1/\xi. \quad (15)$$

Perhaps $c \approx 0.01$ is sufficiently dilute for $\gamma=1$; higher concentrations are allowed for $\gamma < 1$.

C. CALCULATION

The quantity $\langle \sum_{ij} \sigma_i \sigma_j \rangle$ will be evaluated for concentrations satisfying Eq. (15). Hence only a small error will be made by restricting ourselves to the case in which the impurity separation is greater than ξ . In this case the contribution of successive impurities depends only upon whether the number of intervening pure spins is even or odd. This follows from the fact that spins which are separated by ξ or more spins have a correlation approximately equal to $\pm\omega_\infty$. The sign of the correlation is determined by Eq. (12) together with the sign for the pure system. The sign is positive for the pure system if the number of intervening spins is odd and negative otherwise. As stated above, for $\gamma=0$ the counting process results in superparamagnetism and is an analog to a random walk

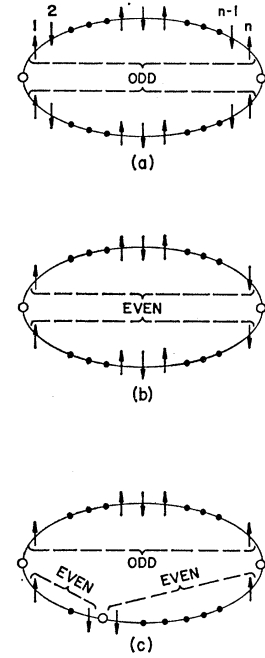


FIG. 1. Examples of impurities in an antiferromagnetic linear chain. The open circles represent impurities.

with restricted reversals.⁹ It is reasonable to expect that the long-range order gives rise to a similar effect for $\gamma \neq 0$. Consider the cases illustrated in Fig. 1.

(1) Case illustrated in Fig. 1(a): In this case there are two impurities. They are separated by an odd number of spins on each side.

$$\langle \sum_j \sigma_1 \sigma_j \rangle = \langle \sum_j \sigma_n \sigma_j \rangle = 1 + \omega_\infty \\ = S_0 + 2\omega_\infty, \quad (16)$$

$$\langle \sum_j \sigma_2 \sigma_j \rangle = \langle \sum_j \sigma_{n-1} \sigma_j \rangle = 1 + 2\omega_1 - \omega_\infty \\ = S_1 - 2\omega_\infty, \quad (17)$$

$$\langle \sum_j \sigma_3 \sigma_j \rangle = 1 + 2\omega_1 + 2\omega_2 + \omega_\infty \\ = S_2 + 2\omega_\infty, \quad (18)$$

where

$$S_n = 1 - (-1)^n \omega_\infty + 2 \sum_{l=1}^n \omega_l, \quad (19)$$

$$S_0 = 1 - \omega_\infty. \quad (20)$$

The result of summing over the entire chain is twice that of the top row or

$$\langle \sum_{ij} \sigma_i \sigma_j \rangle = 2 \left(2 \sum_{n=0}^{\infty} S_n \right) + 4\omega_\infty. \quad (21)$$

In obtaining this result one must take into account that the separations are odd; otherwise the contributions proportional to ω_∞ will cancel out as they do when Eqs. (16) and (17) are added. The S_n 's that appear above are the same partial sums that are important in discussing the ordering of the chain without

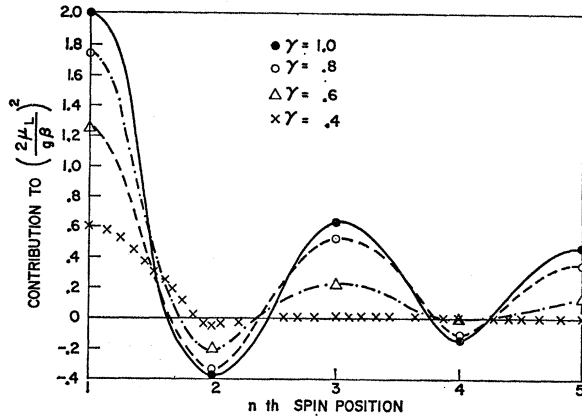


FIG. 2. Contribution to the square of the localized moment μ_L divided by $(g\beta/2)^2$ from the spins n places away from an impurity versus n . The quantity is plotted for various values of γ .

impurities.⁴ From certain reasonable conjectures it was shown that

$$S_1 \leq S_3 \leq \dots \leq 0 \leq \dots \leq S_4 \leq S_2. \quad (22)$$

These conjectures include Eq. (11) and provide a general description of the ordering. The proof of Eq. (22) was based on an expansion of the susceptibility similar to Eq. (6). Equation (22) unlike Ref. 4 includes the possibility of equality. This correction is necessary for Ising coupling. Values for S_n for various anisotropies were calculated which are consistent with Eq. (22). The S_n 's have the property of decreasing rapidly in magnitude with increasing n and alternating in sign. The upper index in the sum should be of order ξ , but the error made in extending the sum to infinity is probably small because of the rapid decrease of S_n .

(2) Case illustrated in Fig. 1(b): There are two impurities but they are separated on each side by an even number of pure spins. In this case

$$\langle \sum_{i,j=1}^N \sigma_i \sigma_j \rangle = 2 \left(2 \sum_{n=1}^{\infty} S_n \right). \quad (23)$$

(3) Case illustrated in Fig. 1(c): There are three impurities separated as shown in Fig. 1(c). Counting as before one obtains

$$\langle \sum_{ij} \sigma_i \sigma_j \rangle = 3 \left(2 \sum_{n=1}^{\infty} S_n \right) + \omega_{\infty}. \quad (24)$$

These special cases can be generalized to

$$\langle \sum_{ij} \sigma_i \sigma_j \rangle = 2q \sum_{i=1}^{\infty} S_i + r^2 \omega_{\infty}, \quad (25)$$

where q is the number of impurities and r is an integer which is determined as follows: The integer r is the distance from the origin after q steps of unit length. Start with any impurity and count clockwise around the chain. The first step is in the positive direction if the number of spins to the next impurity is odd or

in the negative direction if even. The next step is in the same direction as the previous one if the number of spins to the following impurity is odd and in the reverse direction if the number is even. Continue this process until the initial impurity is reached. The result of averaging this process over impurity positions is that of a random walk with restricted reversals. There is a concentration dependence as discussed in Ref. 9 which makes the probabilities of taking a step in the same direction or in the reverse direction unequal. This difference is proportional to c and will be neglected here. Then the problem reduces to that of the usual random walk, and

$$\langle r^2 \rangle_{\text{av imp}} = q, \quad \langle r^4 \rangle_{\text{av imp}} = 3q^2.$$

where $\langle \rangle_{\text{av imp}}$ indicates an average over impurity positions. Hence, Eq. (25) when averaged over impurity positions becomes

$$\langle \langle \sum_{ij} \sigma_i \sigma_j \rangle \rangle_{\text{av imp}} = q \left(2 \sum_{i=0}^{\infty} S_i + \omega_{\infty} \right), \quad (26)$$

and

$$\begin{aligned} \langle \langle \sum_{ij} \sigma_i \sigma_j \rangle^2 \rangle_{\text{av imp}} \\ = q^2 \left(4 \left(\sum S_i \right)^2 + 4\omega_{\infty} \sum S_i + 3\omega_{\infty}^2 \right). \end{aligned} \quad (27)$$

An examination of the steps leading to Eq. (26) shows that the two terms on the right of Eq. (26) arise in quite different ways. The first term is a local contribution. It is independent of the impurity positions for small concentrations and arises from the contributions of spins near an impurity. Its form is not dependent on the size of the system. If the contribution is viewed as a single localized moment μ_L , then spins n places away from an impurity contribute $2(g\beta/2)^2 S_{n+1}$ to the square of μ_L . The factor of 2 arises from the fact that on a chain there are two spins n places away from an impurity. In Fig. 2, the individual contributions $2S_{n+1}$ to μ_L are plotted as a function of the distance n away from an impurity for different values of γ . The nearest neighbors contribute positively, whereas the second neighbors contribute negatively. At present there are values available for S_n only for n up to 4. These values are tabulated in Ref. 4. From Fig. 2 one sees that the contributions to μ_L are largest and least localized for Heisenberg coupling, i.e., $\gamma=1.0$. For Heisenberg coupling the spins five places away from an impurity still make a significant contribution to μ_L , while for smaller γ , μ_L is more localized. For $\gamma \leq 0.4$ only the nearest and next-nearest neighbors make a significant contribution.

The second term of Eq. (26) is nonlocalized. It has the simple form of Eq. (21) only if the impurities are randomly distributed and if the system is finite. Figure 3 shows the function $\langle \langle \sum_{ij} \sigma_i \sigma_j \rangle \rangle_{\text{av imp}} / q$ and its local and nonlocal components as a function of the anisot-

ropy. For the localized part the value of

$$2 \sum_{n=0}^4 S_n,$$

has been used since values of S_n for higher n are not available. Unfortunately, for small anisotropies, $\gamma \sim 1$, this is a rather inaccurate estimate because as discussed above μ_L extends past this range.

III. NEXT-ORDER TERM IN H FOR HEISENBERG COUPLING

Consider the term $\langle \sum \sigma_i \sigma_j \sigma_k \sigma_l \rangle$ which appears in Eq. (6) for the case $\gamma=1.0$; i.e., Heisenberg coupling. It is extremely probable that $\omega_\infty=0$ in this case. Hence spins separated by a distance ξ or more are uncorrelated. This implies that they are statistically independent. Consider the types of terms contributing to the four spin correlations.

(1) One of the spins, i for example, is separated from the others by a distance of at least ξ from the others. Then since it is statistically independent,

$$\langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle = \langle \sigma_i \rangle \langle \sigma_j \sigma_k \sigma_l \rangle = 0. \quad (28)$$

The last equality follows from the fact that $\langle \sigma_i \rangle = 0$.

(2) Two of the spins, i and j , are separated from the other two and from any impurity by a distance of at least ξ . Using the statistical independence of i and j from k and l one obtains

$$\sum'_{ij} \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle = \langle \sigma_k \sigma_l \rangle \left[\sum'_{ij} \langle \sigma_i \sigma_j \rangle \right]. \quad (29)$$

The ($'$) is used here and in subsequent sections to denote restrictions on a sum. The restrictions are different in different sections but are defined in the text. Since i and j are not within ξ of an impurity,

$$\sum'_{ij} \langle \sigma_i \sigma_j \rangle = \sum_{ij} \langle \sigma_i \sigma_j \rangle \quad (30)$$

of the pure system. In Ref. 4 it was shown that this sum is proportional to the temperature T times the zero-field susceptibility χ . The quantity $|J|\chi$ goes to a limit L for $kT/|J| \ll 1$. Hence,

$$\lim_{kT/|J| \rightarrow 0} T\chi = \lim_{kT/|J| \rightarrow 0} LT/|J| = 0. \quad (31)$$

Therefore, these terms do not contribute.

(3) Two of the spins are near one impurity and separated from the others by a distance of at least ξ . The other two are near another impurity. Using the symmetry of the situation and the statistical independence

$$\sum' \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle = 3q(q-1) (\sum' \langle \sigma_i \sigma_j \rangle)^2. \quad (32)$$

The sum is restricted so that i and j are near one

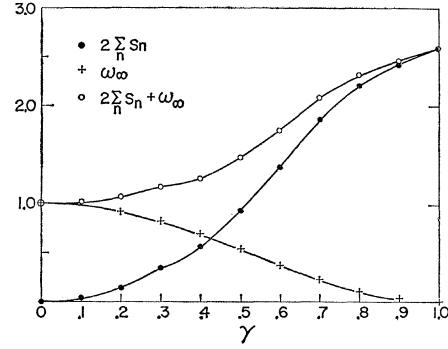


FIG. 3. Graph of

$$2 \sum_{n=0}^4 S_n + \omega_\infty, \quad 2 \sum_{n=0}^4 S_n, \quad \text{and} \quad \omega_\infty$$

as a function of the anisotropy γ .

impurity. The coefficient counts the number of ways in which this situation can occur. The factor of three arises from the fact that index i can be grouped with either j , k , or l . The factor of $q(q-1)$ counts the number of ways the pairs of spins can be near different impurities. The right side of Eq. (32) has been evaluated in Eq. (27). Thus,

$$\sum' \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle = 3q(q-1) \left(2 \sum_{i=1}^{\infty} S_i \right)^2. \quad (33)$$

(4) All the spin indices in the sum are within a distance ξ from one another. If they are not near an impurity the contribution is proportional to $T/|J|$ times the coefficient of the H^3 term in the magnetization of the pure system. This case does not contribute for $kT/|J| \ll 1$. Hence, it is only necessary to consider the situation when all four indices are near the same impurity. One could try to express this sum in terms of the pure four-spin correlations by an assumption similar to that made for the two-spin case. In order to make any statements about the total sum arising from the cases considered above, one would have to compare the two-spin and four-spin correlations of the pure system. Not enough is known about these correlations to make such a comparison. As an alternative approach, we shall assume

$$\sum'_{ijkl} \langle \sigma_i \sigma_j \sigma_k \sigma_l \rangle = \left(\sum' \langle \sigma_i \sigma_j \rangle \right) \left(\sum' \langle \sigma_k \sigma_l \rangle \right) \quad (34)$$

$$= \left(2 \sum_{n=1}^{\infty} S_n \right)^2. \quad (35)$$

The sums are restricted to be near a single impurity. Because the spins are within a distance ξ of one another they are statistically dependent. Hence, Eq. (34) is an assumption and has not been proven. This contribution is a factor of 3 smaller than that of case (3). Thus,

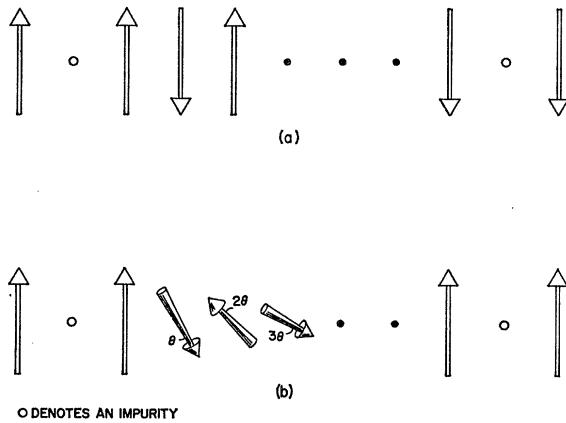


FIG. 4. Classical model for interpreting the Heisenberg result.

the result does not depend too critically on Eq. (34.) One can show that for Heisenberg coupling the magnetization is proportional to q without using Eq. (34).

Combining all these contributions to the sum of the four spin correlations the magnetization can be written

$$\frac{4kTM}{q(g\beta)^2H} = 2 \sum_{i=1}^{\infty} S_i - \frac{1}{3} \left(\frac{g\beta H}{2kT} \right)^2 (2 \sum_{i=1}^{\infty} S_i)^2 + \dots \quad (36)$$

The magnetization is that of q localized, noninteracting spins having $S^z = \pm \frac{1}{2}$ and a magnetic moment $\mu_L = (2 \sum S_i)^{1/2} g\beta/2$. The free-spin behavior can be interpreted classically. For a small concentration of impurities there is no increase in exchange energy in reversing the direction of a given localized moment. Consider two oppositely directed localized moments as in Fig. 4(a). This spin configuration is approximately degenerate with the one shown in Fig. 4(b). The localized moments can line up parallel if the intermediate spins form something resembling a Bloch wall. Interpreting the spins classically, if each spin is tilted with respect to the next one by an angle θ as shown in Fig. 4(b), the increase in the exchange energy necessary to line up the localized moments is

$$\delta E_{\text{ex}} = J(\pi/2)^2 n^{-1}, \quad (37)$$

where n is the number of spins separating the localized moments. For small concentrations, $n \rightarrow \infty$, and it requires no increase in exchange energy to reverse the direction of a localized moment.

IV. THE GENERAL CASE OF ANISOTROPIC COUPLING

If $\gamma \neq 1$, the above treatment of the second-order term is no longer valid. Because $\omega_{\infty} \neq 0$, spins separated by a distance greater than ξ are no longer statistically independent. The classical explanation given above also breaks down for $\gamma \neq 1$ because if there is anisotropy then δE_{ex} does not go to zero for large separations. It is likely that in the general case the impurity magnetization is approximately the sum of a contribution of q localized moments of magnitude $g\beta(2 \sum S_i)^{1/2}/2$ and a single moment of magnitude $g\beta(\omega_{\infty} q)^{1/2}/2$. The second contribution saturates in small fields to the value $g\beta(\omega_{\infty} q)^{1/2}/2$ and is a generalization of the superparamagnetism of Ref. 9.

V. CONCLUSIONS

The properties of a linear antiferromagnetic chain containing ferromagnetically coupled impurities depend strongly upon the anisotropy. In the low-temperature limit for Ising coupling and near the Ising limit the system is a superparamagnet.

There is a contribution to the magnetization which is localized near each impurity. For the present model this local contribution μ_L is equal to $g\beta(2 \sum S_n)^{1/2}/2$. The quantity μ_L becomes increasingly localized and goes to zero with increasing anisotropy. The localized contribution remains as $kT/|J| \rightarrow 0$. To the author's knowledge, it is the first case of paramagnetic or free-spin behavior in a strongly coupled exchange system. By measuring the magnetic-field dependence of the magnetization, the two contributions can be separated. In the case of Heisenberg coupling, the absence of a superparamagnetic contribution can be used as an experimental test to see if $\omega_{\infty} = 0$. The experimental results⁷ on the organic free radicals are consistent with the paramagnetism predicted in the case of Heisenberg coupling. The data is insufficient to provide a thorough test.

The restriction to finite size systems is not necessary in the case of Heisenberg coupling. The superparamagnetic contribution does not saturate in a magnetic field as completely if the correlations do not extend over the entire system. This situation arises for larger systems or higher temperatures.

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