

## Note on Critical Concentrations in Magnetism

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In a recent paper, the Bethe-Peierls-Weiss (BPW) method has been applied to the problem of dilute magnetism, taking into account the fluctuation in the number of magnetic atoms interacting with the BPW cluster. The results given differ considerably from those of Smart who assumed a uniform molecular field. We show that this difference is due to an error in the former calculation and prove that fluctuations of a general kind in the molecular field have no effect upon the BPW result.

IN several recent papers,<sup>1-3</sup> various extensions of the Bethe-Peierls-Weiss (BPW) method have been proposed in order to treat the behavior of a magnetic system diluted by a nonmagnetic component. In particular, Smart has taken into account the fluctuations in the number of magnetic atoms in the "first shell" of the BPW cluster. In his treatment, Smart approximates the interaction of the cluster with its surroundings by assuming a uniform internal field  $H_1$  which acts on the outer magnetic atoms. It is evident that such a procedure takes no account of the fluctuations in number and location of magnetic atoms which surround and interact with the first shell.

In an extension<sup>3</sup> of Smart's calculation, it is assumed that the molecular field acting on the  $i$ th magnetic atom in the first shell is proportional to  $n_i$ , where  $n_i$  is the number of magnetic neighbors it has outside the cluster. By this means, one hopes to take approximate account of the fluctuations mentioned above. The results given in reference 3 for the critical concentration needed for ferromagnetism are considerably larger than those of Smart and others.<sup>1,2,4</sup> We shall see, however, that there is an error in the calculation and that the corrected calculation gives results for the Curie temperature and critical concentration identical to those of Smart.

In this paper we prove a more general result, namely, that the BPW Curie point is independent of fluctuations of any type in the magnitude of the molecular fields, provided they do not depend on the spins or location of magnetic atoms within the cluster. This last proviso is satisfied in Smart's treatment and in its extension.

Our notation is essentially that of Brown and Luttinger<sup>5</sup> with the following additions. Let  $x_j=1$  or 0 depending on whether the  $j$ th atom of the cluster is magnetic or nonmagnetic, and let  $h_j$  be proportional to the molecular field acting on the  $j$ th atom in the first shell. Then the cluster partition function is

$$Z_{cl} = \int d\Omega_0 \exp(x_0 \lambda_0 \cdot \mathbf{S}_0) \prod_{i=1}^z P_i, \quad (1)$$

where

$$P_i = \int d\Omega_i \exp[(2p x_0 \mathbf{S}_0 + h_i \lambda_1 + \lambda_2) \cdot x_i \mathbf{S}_i]. \quad (2)$$

Note the presence in (2) of  $\lambda_2$  which is proportional to a fictitious external field acting on the shell atoms. This field, assumed parallel to  $\lambda_0$  (and  $\lambda_1$ ), is introduced for reasons that will soon be apparent. If we let  $\lambda_2=0$  and  $h_j=1(n_j)$ , we arrive at the cluster partition function assumed by Smart (Charap).

The cluster partition function to second order in  $\lambda_1$  and  $\lambda_2$  and first order in  $\lambda_0$  is

$$Z_{cl} = C \left\{ \prod_{j=1}^z \alpha_{0j} \right\} \left\{ 1 + \frac{S^2}{6} [2x_0 \lambda_0 \mathcal{L} \sum_j \phi_j + \sum_j \phi_j^2 + x_0 \mathcal{L}^2 \sum_{i \neq j} \phi_i \phi_j] \right\}, \quad (3)$$

where  $C$  is a constant and

$$\begin{aligned} \alpha_{0j} &\equiv \alpha(x_0 x_j 2p S^2), \\ \mathcal{L} &= \mathcal{L}(2p S^2), \\ \phi_j &= (h_j \lambda_1 + \lambda_2) x_j. \end{aligned}$$

The total partition follows from

$$\begin{aligned} \ln Z &= N \sum_{x_i, h_i} P(x_0 \cdots x_z, h_1 \cdots h_z) \ln Z_{cl} \\ &\equiv N \langle \ln Z_{cl} \rangle. \end{aligned} \quad (4)$$

Here  $P$  is the joint probability of the  $x_j$ 's and  $h_j$ 's. For the following, we assume that the magnetic atoms are distributed uniformly with concentration  $c$ . Furthermore, we assume that the  $h_j$ 's have the same mean value  $\langle h \rangle$  and are independent of the  $x_k$ 's. They may be statistically dependent on each other, as in reference 3, where  $h_j = n_j$ .

The average moment  $\langle m_0 \rangle$  of magnetic atoms which occupy the central position of clusters is, of course, given by

$$\lim_{\lambda_0, \lambda_2 \rightarrow 0} (\partial \ln Z / \partial \lambda_0) = N \langle x_0 m_0 \rangle = N c \langle m_0 \rangle, \quad (5)$$

and the average "first shell" magnetic moment  $\langle m_1 \rangle$

<sup>1</sup> H. Sato, A. Arrott, and R. Kikuchi, *J. Phys. Chem. Solids* **10**, 19 (1959).

<sup>2</sup> J. S. Smart, *J. Phys. Chem. Solids* **16**, 169 (1960).

<sup>3</sup> S. H. Charap, *Phys. Rev.* **126**, 1393 (1962).

<sup>4</sup> R. J. Elliot, *J. Phys. Chem. Solids* **16**, 165 (1960).

<sup>5</sup> H. A. Brown and J. Luttinger, *Phys. Rev.* **100**, 685 (1955).

follows from

$$\lim_{\lambda_0, \lambda_2 \rightarrow 0} (\partial \ln Z / \partial \lambda_2) = N \sum_j \langle x_j m_j \rangle = N c z \langle m_1 \rangle. \quad (6)$$

Thus,  $\lambda_2$  was introduced to simplify the computation of  $\langle m_1 \rangle$ . We note also that, for  $h_j = n_j$ ,

$$\frac{1}{N z c} \lim_{\lambda_0, \lambda_2 \rightarrow 0} \frac{\partial \ln Z}{\partial \lambda_1} = - \frac{1}{z c} \sum_j \langle x_j n_j m_j \rangle = \langle n_1 m_1 \rangle. \quad (7)$$

The first-shell magnetic moment cannot be determined from (7) unless  $n_1$  and  $m_1$  are uncorrelated, i.e., unless

$$\langle n_1 m_1 \rangle = \langle n_1 \rangle \langle m_1 \rangle. \quad (8)$$

Since, however, the internal field on the  $i$ th atom is proportional to  $n_i$ , the random variables  $n_i$  and  $m_i$  are correlated except in the case  $c=0$  or 1. This correlation is neglected in reference 3 and invalidates the results therein. We now proceed to show that the correct result is independent of the concentration fluctuations in the second shell.

Using (3)-(6) we find, for small  $\lambda_1$  (near the Curie

temperature),

$$\begin{aligned} \langle m_0 \rangle &= \frac{1}{3} S^2 \lambda_1 z c \mathcal{L} \langle h \rangle, \\ \langle m_1 \rangle &= \frac{1}{3} S^2 \lambda_1 [1 + \mathcal{L}^2 c^2 (z-1)] \langle h \rangle. \end{aligned} \quad (9)$$

By the usual procedure of equating  $\langle m_0 \rangle$  and  $\langle m_1 \rangle$ , we arrive at Smart's result,

$$\mathcal{L}(2JS^2/kT_c) = 1/c(z-1). \quad (10)$$

We remark, incidentally, that only the mean and variance of the distribution of magnetic atoms in the first shell enters into the calculation, the results being independent of higher moments of the distribution. In a similar way, only the mean, or first moment of the distribution of molecular fields (which may be thought of as arising from magnetic atoms in the second shell), enters when the molecular field is allowed to fluctuate. We conclude that proper account of the fluctuations in the second shell within the BPW scheme would probably involve enlarging the BPW cluster.

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Nuclear Magnetic Resonance in the Demagnetized State

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A discussion is given of experimental results and theoretical considerations which apply in the case of complete adiabatic demagnetization in the rotating frame (ADRF) for nuclear spin systems in solids. Although the net magnetization in this state is zero, both continuous wave and pulse signals are predicted and readily observed at the normal resonance frequency. These signals appear to be much like the derivative of the signals observed in the normal nuclear magnetic resonance (NMR) cases with amplitudes comparable to normal NMR signal amplitudes and they persist for times comparable with  $T_1$  at high fields even when the line is purely homogeneously broadened. A simple heuristic theory is used to calculate, after ADRF, the shape of the free-induction decay and the form of the absorption at  $\omega \approx 0, \Omega$ , and  $2\Omega$ , where  $\Omega$  is the resonance frequency of the spin system. The density matrix method is then used to calculate line shapes and free-induction decay signals which are found to be in agreement with experiment and the heuristic model calculation. The concept of spin temperature is used to calculate the effect of applying an rf field to produce a line asymmetry in a homogeneously broadened system. It is also shown that, in general, the free induction decay signal is not the Fourier transform of the line shape and homogeneously broadened lines do not saturate uniformly. In addition, it is found experimentally that ADRF is reversible, spin systems are coupled, spectra at low frequency and double the resonance frequency are observed, and spin-system relaxation times vary rapidly with field at low dc fields but are of order of  $T_1$  at high fields.

I. INTRODUCTION

THE technique of adiabatic demagnetization has been used in many experiments,<sup>1</sup> the most common one being that in which a lattice containing

magnetic spins is cooled to very low temperatures. After adiabatic demagnetization the previous large applied dc field is replaced by the random local internal dipole or exchange fields due to neighboring magnetic

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<sup>1</sup> See, for example, C. B. Garrett, *Magnetic Cooling* (Harvard

University Press, Cambridge, Massachusetts, 1954); A. Abragam and W. G. Proctor, *Phys. Rev.* **109**, 1441 (1958); L. C. Hebel and C. P. Slichter, *ibid.* **107**, 901 (1957).