ues of $E_{exc}{}^4$ and $E_{exc}{}^3$ at 4.1 K are about $\frac{1}{3}$ of their values at 80 K. The dependence of E_{exc} on temperature is consistent with theoretical predictions. E_{exc} at low temperatures can be expressed in the form[4]

$$E_{exc}(T) = E_{4f}{}^{eff} - E_F(T) = E_{4f}{}^{eff} - c(z+p)^{2/3}, \quad (7)$$

where $E_{4f}{}^{eff}$ is independent of p or temperature, c is a positive constant, and z is the number of conduction electrons per ion for $p=0$. The values of $E_{exc}{}^M$ for the $Eu_xLa_{1-x}Rh_2$ compounds were found to be positive (except for $E_{exc}{}^4$ of $x=0.075$) and p therefore decreases with temperature. According to Eq. (7) such a decrease will cause $E_{exc}{}^M$ to be an increasing function of temperature, as found from our analysis of the experimental results.

In the analysis of the experimental results, it was assumed that the widths of all the moving lines do not change as a function of temperature, and that they are equal to the linewidth in the absence of fluctuation phenomena. This assumption implies that the characteristic fluctuation time between the $4f$ localized level and the conduction band is shorter than 4×10^{-11} sec. Such short fluctuation times are consistent with the values of 100 K found for the widths of the localized $4f$ level. Such a width corresponds to a lifetime of 10^{-13} sec.

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[1]D. K. Wohlleben and B. R. Coles, in *Magnetism*, edited by H. Suhl (Academic, New York, 1973), Vol. V, p. 3.

[2]L. L. Hirst, Phys. Kondens. Mater. 11, 255 (1970), and to be published.

[3]E. R. Bauminger, D. Froindlich, I. Nowik, S. Ofer, I. Felner, and I. Mayer, Phys. Rev. Lett. 30, 1053 (1973).

[4]J. M. Robinson and P. Erdos, Phys. Rev. B 8, 4333 (1973).

New Type of Phase Transition

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It is shown that the ferromagnetic Ising model on a Cayley tree lattice exhibits a new type of phase transition at the field $B=0$ below the Bethe-Peierls transition temperature T_{BP}. The leading nonanalytic part of the free energy is of the form B^κ, where the "critical" exponent $\kappa(T)$ increases smoothly from one to infinity as the temperature goes from 0 to T_{BP}. This implies a transition of "continuous" order κ.

The self-consistent Bethe-Peierls (BP) treatment[1] has been believed to be exact for the ferromagnetic Ising problem on a Cayley tree (also called Bethe lattice).[2] Only recently Eggarter[3] found that the corresponding free energy at zero magnetic field is an analytic function of the temperature, thus implying no phase transition in contrast to the BP treatment. As pointed out in Ref. 3, the explanation of the apparent paradox is the unusual topological structure of a large Cayley tree: Not only is a finite portion of its sites on the surface, but the "interior" of a Cayley tree, i.e., all sites a sufficient distance away from the surface, actually contains an arbitrarily small portion of all the sites. The BP transition, in fact, takes place only in the "interior" and disappears if the bulk properties are calculated in the proper thermodynamic limit.

In this paper we shall prove that the bulk behavior of the Ising model on a Cayley tree nevertheless displays a phase transition, but an unusual one. The transition is seen only in the field dependence of the free energy and becomes arbitrarily weak, if the Bethe-Peierls transition temperature T_{BP} is approached from below. Since this transition smoothly interpolates between a first-order transition at $T=0$ and an infinite-order transition at T_{BP}, it might be called a continuous transition.

First we derive a closed expression for the free energy per site in the thermodynamic limit. For simple notation we use a reduced temperature, $t=(\beta J)^{-1}$, where $J>0$ is the nearest neighbor coupling, and a reduced magnetic field $b=\beta\mu B$. In these variables the partition function is given by

$$Z(t,b)=\sum_{\{\sigma_i=\pm1\}}\exp(b\sum_i\sigma_i+t^{-1}\sum_{\langle i,j\rangle}\sigma_i\sigma_j). \qquad (1)$$

Let $K\geq 2$ be the connectivity of the Cayley tree. (The linear chain, $K=1$, is well known and is omitted here.) Following Eggarter[3] we consider an n-generation branch. It is defined as an initial site connected to K $(n-1)$-generation branches; a 1-generation branch is a single site. Let $Z_n^{\pm}$ be the sum of all contributions to the partition function of an n-generation branch with initial site spin up (+) or down (−). Then the recurrence relations

$$Z_{n+1}^{\pm}=e^{\pm b}[Z_n^{+}e^{\pm1/t}+Z_n^{-}e^{\mp1/t}]^k,\; Z_1^{\pm}=e^{\pm b} \qquad (2)$$

are easily derived.[3] For the ratio $Z_n^+/Z_n^-=\exp(2x_n)$ one obtains from (2) the relation

$$x_{n+1}=b+\tfrac{1}{2}K\ln\{[\exp(2x_n+2/t)+1]/[\exp(2x_n)+\exp(2/t)]\},\quad x_1=b. \qquad (3)$$

Since the right-hand side is bounded in x, it follows that Z_n^+/Z_n^- is finite for $n\to\infty$ and thus

$$Z_n=Z_n^++Z_n^-\sim Z_n^{\pm}\sim(Z_n^+Z_n^-)^{1/2}$$

in the thermodynamic limit.

The relations (2) can be solved in terms of x_n. In particular, one finds

$$\ln(Z_{n+1}^+Z_{n+1}^-)=K\ln(Z_n^+Z_n^-)+K\ln\{[\exp(1/t)+\exp(-2x_n-1/t)][\exp(1/t)+\exp(2x_n-1/t)]\}$$
$$=\sum_{m=1}^{n}K^{n+1-m}\ln[\exp(2/t)+\exp(-2/t)+\exp(2x_m)+\exp(-2x_m)].$$

To calculate the free energy we consider an n-generation branch.[4] The total number of sites on the branch is

$$N_n=\sum_{m=0}^{n-1}K^m=(K^n-1)/(K-1).$$

If F_n denotes the free energy, we obtain

$$f(t,b)=-\lim_{n\to\infty}\frac{\beta F_n}{N_n}=\tfrac{1}{2}(K-1)\lim_{n\to\infty}K^{-n}\ln(Z_n^+Z_n^-)$$
$$=\tfrac{1}{2}(K-1)\sum_{m=1}^{\infty}K^{-m}\ln[\exp(2/t)+\exp(-2/t)+\exp(2x_m)+\exp(-2x_m)]. \qquad (4)$$

For zero field, obviously $x_n=0$ and we obtain Eggarter's result: $f(t,0)=\ln(e^{1/t}+e^{-1/t})$. Here we are interested in the b dependence of f and therefore we consider

$$\Delta f(t,b)=f(t,b)-f(t,0)=\tfrac{1}{2}(K-1)\sum_{n=1}^{\infty}K^{-n}\ln\left(1+\frac{\sinh^2x_n}{\cosh^2t^{-1}}\right). \qquad (5)$$

Relation (3) is rewritten as

$$x_{n+1}=b+h(x_n),\quad x_1=b, \qquad (6)$$

$$h(x)=\tfrac{1}{2}K\ln\{[1+(\gamma/K)\tanh x][1-(\gamma/K)\tanh x]^{-1}\} \qquad (7)$$

with the parameter $\gamma(t)=K\tanh t^{-1}$; $t_{\rm BP}$ is then defined by $\gamma(t_{\rm BP})=1$.

As it is known that f is analytic in b except at $b=0$,[5] we shall investigate Δf for small b. The following properties will be proved[6]:

(α) The free energy is analytic at $b=0$ for all $t>t_{\rm BP}$.

(β) The free energy is nonanalytic at $b=0$ for all $t<t_{\rm BP}$. The b dependence can be represented by the asymptotic expansion

$$\Delta f=\sum_{l=1}^{\infty}a_l(t)b^{2l}+A(t)|b|^{\kappa}\{1+c_1(t)|b|+c_2(t)b^2+\dots\}. \qquad (8)$$

Here $a_l = \bar{a}_l(t)(1-\gamma^{2l}/K)^{-1}$ diverges at the temperature $t = t_{2l}$ given by $\gamma(t_{2l}) = K^{1/2l}$ ($t_2 < t_4 < \ldots < t_\infty = t_{\rm BP}$) and the "critical" exponent,

$$\kappa(t) = \ln K/\ln\gamma(t), \qquad (9)$$

smoothly increases from 1 to ∞ as t goes from 0 to $t_{\rm BP}$. In particular, the expansion (8) implies the following:

(β1) For $t > t_{2l}$ the l leading terms are regular of the form

$$(\Delta f)_{\rm reg} = \sum_{m=1}^{l} [\bar{a}_m/(1-\gamma^{2m}/K)]b^{2m} \qquad (10)$$

such that the coefficient of b^{2l} diverges as $t \to t_{2l}$ from above.

(β2) The leading nonanalytic term $A|b|^\kappa$ is dominant only for temperatures $0 \le t < t_2$, where $1 \le \kappa < 2$, whereas in the range $t_{2l} < t < t_{2l+2}$, where $2l < \kappa < 2l+2$, it succeeds the l regular terms of (β1).

(β3) For $t = t_{2l}$ ($l = 1, 2, \ldots$) both $a_l(t)$ and $A(t)$ diverge and the leading nonanalytic term is $\bar{a}_l(t_{2l})(2l/\ln K)b^{2l}\ln(1/|b|)$.

To prove these statements we first notice that the analytic structure of the free energy (5) near $b = 0$ is closely related to how the x_n vary with b for large n. The crucial quantity controlling this behavior is the derivative $h'(0) = \gamma$ of the function h in Eq. (7).

For $\gamma < 1$ ($t > t_{\rm BP}$) the map given by the iteration procedure (6) is contracting for sufficiently small values of x_n. Simple inspection yields the estimate $|h'(x)| \le (1+\gamma)/2 < 1$, if $4|x|^2 \le 1-\gamma$ (x complex). With the standard methods for proving Banach's fixed-point theorem it follows that for (complex) b within the circle $|b| \le (1-\gamma)^{3/2}/4 = \epsilon(\gamma)$ the $x_n(b)$ always remain in the region $4|x_n|^2 \le 1-\gamma$ and converge uniformly towards an $x_\infty(b)$ which then is analytic in b. This ensures that the free energy (5) is analytic at least in the circle $|b| < \epsilon(\gamma)$ and proves statement (α).

For $\gamma > 1$ ($t < t_{\rm BP}$) the iteration (6) obviously is unstable around $b = 0$. While $x_n(b=0) = 0$, the sequence x_n for arbitrarily small $|b| > 0$ converges to a finite value $x_\infty(b)$, which for $b = |b|e^{i\varphi}$ explicitly depends on φ (the cases $\varphi = 0$, $\pi/2$, π can be checked easily). Thus, x_n certainly does not converge uniformly in any neighborhood of $b = 0$ which suggests a nonanalytic behavior of Δf around $b = 0$. In order to work out the nonanalyticities explicitly we inspect the formal expansion of Δf in powers of b^2. Since $h(x)$ is an odd function, $x_n(b)$ also is odd and its expansion is

$$x_n(b) = \sum_{l=1}^{\infty} x_n^{(2l-1)} b^{2l-1}. \qquad (11)$$

From Eq. (6) we obtain a sequence of linear recurrence relations for the expansion coefficients $x_n^{(2l-1)}$. The first one is $x_{n+1}^{(1)} = 1 + \gamma x_n^{(1)}$ ($x_1^{(1)} = 1$), with the solution

$$x_n^{(1)} = (\gamma^n - 1)/(\gamma - 1). \qquad (12)$$

The next relation is

$$x_{n+1}^{(3)} = \gamma x_n^{(3)} - \tfrac{1}{3}\gamma[1-(\gamma/K)^2](x_n^{(1)})^3, \quad x_1^{(3)} = 0.$$

As we are interested only in the dominant contribution for large n which is generated by the inhomogeneous term, we get from (12) $x_n^{(3)} = O(\gamma^{3n})$. Similarly, the leading term of the higher order coefficients is $x_n^{(2l-1)} = O(\gamma^{2l-1})$. Expanding the free energy as

$$\Delta f = \sum_{l=1}^{\infty} a_l b^{2l}$$

one finds that the most dangerous contribution to a_l is the geometric series $\sum_n K^{-n}\gamma^{2ln}$ which converges only for $\gamma^{2l} < K$, i.e., $t > t_{2l}$. This proves (β1). In addition we note that the a_1 can be calculated successively. The first coefficient is easily derived,

$$a_1(t) = (1+\gamma/K)^2/[2(1-\gamma^2/K)], \qquad (13)$$

which corresponds to the susceptibility, also calculated recently in Ref. 7.

The next step is to modify the above expansion such that the divergence in a_l for $t \le t_{2l}$ is removed. Intuitively, this is achieved via the following cutoff argument. Using the expansion (11) term by term to calculate the free energy to increasing orders in b ceases to make sense as soon as $x_n^{(2l-1)}b^{2l-1}$ is of order 1. This happens (for all l) when $\gamma^n b = O(1)$ or for $n \sim n_0(b) = \ln|b|^{-1}/\ln\gamma$. If a contribution to the free energy resulting from a formal expansion into powers of b diverges, the influence of the higher order terms in Eq. (11) can be sensibly replaced by cutting off the summation at $n = n_0(b)$. The result of this procedure is that for $t < t_{2l}$ the most divergent contribution to $a_l b^{2l}$ is converted into

$$b^{2l}\sum_{n=1}^{n_0(b)} K^{-n}\gamma^{2ln} \sim b^{2l}(\gamma^{2l}/K)^{n_0} = |b|^\kappa, \qquad (14)$$

where $\kappa(t)$ is given by Eq. (9).[8]

It is straightforward to make the above cutoff argument rigorous by putting upper and lower bounds on the singular part of Δf which both display the $|b|^\kappa$ power law exactly. Since $h(x)$ is concave for $x > 0$, an upper bound $\bar{x}_n$ on x_n is given by ($b > 0$)

$$\bar{x}_{n+1} = b + \gamma\bar{x}_n, \quad \bar{x}_1 = b \text{ or } \bar{x}_n = b(\gamma^n - 1)/(\gamma - 1),$$

where the restriction $\bar{x}_n \leqslant b + h(\infty)$ can be imposed, too. An appropriate lower bound $\underline{x}_n$ on x_n is found by considering the recurrence relation for $\exp(2x_n)$. Since, for $\gamma > 1$, $\exp[2h(x)]$ is a convex function of $\exp(2x)$ around $x=0$ and because

$$d \exp[2h(x)]/d\exp(2x)|_{K=0} = \gamma,$$

the linear recurrence relation for $\exp(2\underline{x}_n)$ is

$$\exp(2\underline{x}_{n+1}) = \exp(2b)\{1+\gamma[\exp(2\underline{x}_n)-1]\}, \quad \exp(2\underline{x}_1) = \exp(2b),$$

which can be used up to some finite value $\underline{x}_n \leqslant c(\gamma)$. The logarithm in Eq. (5) is bounded by $(\alpha_{1/2} > 0)$

$$\alpha_1 x^2 \geqslant \ln(1+\sinh^2 x/\cosh^2 t^{-1}) \geqslant \begin{cases} \alpha_2[\exp(2x)-1]^2, & x \leqslant c \\ 0 & , \quad x > c. \end{cases}$$

Inserting $\bar{x}_n$, $\underline{x}_n$ into these bounds completes the proof of (β2) after a little algebra.

At the particular temperatures $t = t_{2l}$ the sum in Eq. (14) has to be performed differently, because $\gamma^{2l}/K = 1$. The result is

$$b^{2l} \sum_{n=1}^{n_0} \left(\frac{\gamma^{2l}}{K}\right)^n = b^{2l}[n_0(b)-1] \sim b^{2l} \ln|b|^{-1}.$$

Again, by considering the bounds described above, it is easily confirmed that this is the exact leading nonregular contribution. One may even calculate the coefficient in front of this term.[9] Since the free energy is regular for $b \neq 0$, the coefficients $a_l(t)$ and $-A(t)$ necessarily have identical singular behavior at $t = t_{2l}$. With $\gamma(t)^{\kappa(t)} = K$ we therefore obtain

$$\lim_{t\to t_{2l}} [a_l(t) b^{2l} + A(t)|b|^\kappa]_{\text{sing}} = \bar{a}_l(t_{2l}) \lim_{t\to t_{2l}} \frac{(b^{2l} - |b|^\kappa)}{(1-\gamma^{2l}/K)}$$

$$= \bar{a}_l(t_{2l})(2l/\ln K) b^{2l} \ln|b|^{-1},$$

which completes the proof of (β3).

We have shown that the Ising model on a Cayley tree exhibits an unusual type of phase transition which one might call a continuous phase transition. It actually consists of a line of phase transitions extending from $t=0$ to $t=t_{\mathrm{BP}}$. At any temperature t in this interval the transition is characterized by the exponent $\kappa(t)$ given by Eq. (9). If one uses an Ehrenfest classification, the transition is of lth order in the interval $t_{l-1} < t \leqslant t_l$ $[\gamma^l(t_l) = K]$. If t approaches $t_\infty = t_{\mathrm{BP}}$ the transition is of infinite order and the nonanalytic part of the free energy fades away. The usual type of phase transition is associated with the appearance of some kind of order which sets in either abruptly (first order) or continuously (second order). The system considered here apparently is not able to establish order except at $t=0$. The line of phase transitions we have found interpolates between the high-temperature disordered state and the zero-temperature ordered state in the most continuous way.

It is evident that the continuous phase transition in our case is a consequence of the topology of the lattice. There is, however, evidence that this type of transition also might occur in more realistic situations. One example is the random Ising ferromagnet on a two- or three-dimensional lattice. Griffiths[10] showed that these systems have a temperature range of nonanalytic field dependence without spontaneous magnetization, although the singular behavior could not be worked out explicitly. Furthermore, a number of two-dimensional models with continuous symmetry are known to show no spontaneous order at nonzero temperatures, but they appear to have a susceptibility which diverges at a finite temperature corresponding to our t_2. It is possible that also in those systems one has a continuous phase transition extending to some $t_\infty > t_2$, like the one described in this paper.

[1]H. A. Bethe, Proc. Roy. Soc., Ser. A 150, 552 (1935).

[2]C. Domb, Advan. Phys. 9, 145 (1960).

[3]T. P. Eggarter, Phys. Rev. B 9, 2989 (1974).

[4]We may equally well consider a Cayley tree by connecting $K+1$ such branches to a central site. In the thermodynamic limit there is no difference.

[5]T. D. Lee and C. N. Yang, Phys. Rev. 87, 404, 410 (1952).

[6]We defer more detailed proofs and further results to a longer paper.

[7]J. von Heimburg and H. Thomas, to be published.

[8]Note that less divergent contributions which are of the type

$$b^{2l}\sum_{n=1}^{n_0} K^{-n}\gamma^{(2l-r)n}$$

give rise to terms like $|b|^{K+r}$.

[9]There is no apparent way to obtain a closed expression for $A(t)$ in Eq. (8).

[10]R. B. Griffiths, Phys. Rev. Lett. 23, 17 (1969).

[11]H. E. Stanley and T. A. Kaplan, Phys. Rev. Lett. 17, 913 (1966); see also L. Reatto, in *Critical Phenomena, Proceedings of the International School of Physics "Enrico Fermi," Course LI,* edited by M. S. Green (Academic, New York, 1972).

Singlet-Singlet Induced-Moment System*

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A new decoupling procedure for the two-level induced-moment system in the paramagnetic regime is described. It offers improvements over the results of other methods and can in principle be extended to other systems.

It is becoming commonplace to study and understand the magnetic properties of rare-earth metals and intermetallic compounds in which the effects of many crystal-field states are significant. These systems are studied theoretically by using a molecular-field approximation,[1] a random-phase approximation (RPA),[2] or, less frequently, the two-site correlation approximation (TSCA).[3] One of the original systems studied was the two-singlet induced-moment system[1-3] in which the two lowest single-ion eigenstates, $|A\rangle$ and $|B\rangle$, of the crystal-field operator V^c are magnetic singlets separated by an energy Δ. All matrix elements of the total magnetic moment operator $\vec{J}_i$ of the ith ion between these two states are zero except for $\langle B|J^z|A\rangle=\alpha$. The Hamiltonian was assumed to be

$$H=-\sum_{ij}K_{ij}\vec{J}_i\cdot\vec{J}_j+\sum_j V_j^c,\quad V^c|A\rangle=0,\quad V^c|B\rangle=\Delta|B\rangle. \tag{1}$$

The collective excitations have been calculated using the RPA and TSCA, and some thermodynamic quantities have been calculated self-consistently. Two points should be noted, one of which will be taken up: (a) The magnetization is double valued as a function of temperature T, in general, which is interpreted as indicating a first-order phase transition. There are arguments that the transition should be second order. (b) The exact excitation spectrum in one dimension has been calculated.[4] It does not agree with RPA or TSCA calculations. Here, a decoupling scheme will be outlined which gives results for the paramagnetic region[4] ($\langle J^z\rangle=0$) which agree closely with the exact result. The extension of it to describe the magnetically ordered region will be treated elsewhere.

For simplicity we shall assume a nearest-neighbor exchange interaction and map the operators $J_j^{\pm}$, J_j^z, and V_j^c onto the components of a pseudospin-$\frac{1}{2}$ operator, $\vec{\sigma}_j$. The eigenstates of σ_j^z are $|\pm\rangle_j$ belonging to eigenvalues $\pm\frac{1}{2}$; we map $|A\rangle\to|+\rangle$ and $|B\rangle\to|-\rangle$, and the Hamiltonian becomes[2,3,5]

$$H=-J\sum_{j\delta}\sigma_j^x\sigma_{j+\delta}^x-\Delta\sum_j\sigma_j^z+\tfrac{1}{2}\Delta N, \tag{2}$$

where $\vec{\delta}$ is a primitive lattice vector and N is the total number of ions. The operators σ_j^x and σ_j^y are two of the single-excitation operators of this system. In the paramagnetic region $\langle\sigma^x\rangle=0$. The equations of motion for the Green's functions are[6]

$$\begin{aligned}
&E\langle\langle\sigma_i^x|B_j\rangle\rangle=g^x(\vec{r}_j-\vec{r}_i)+i\Delta\langle\langle\sigma_i^y|B_j\rangle\rangle,\\
&E\langle\langle\sigma_i^y|B_j\rangle\rangle=g^y(\vec{r}_j-\vec{r}_i)-i\Delta\langle\langle\sigma_i^x|B_j\rangle\rangle+2iJ\sum_\delta\langle\langle\sigma_i^z\sigma_{i+\delta}^x|B_j\rangle\rangle,\\
&g^\nu(\vec{r}_j-\vec{r}_i)=(2\pi)^{-1}\langle[\sigma_i^\nu,B_j]\rangle.
\end{aligned}\tag{3}$$

At this point the RPA replaces $\langle\langle\sigma_i^z\sigma_{i+\delta}^x|B_j\rangle\rangle$ by $\langle\sigma^z\rangle\langle\langle\sigma_{i+\delta}^x|B_j\rangle\rangle$. This approach treats σ_i^z as an approximate constant of the motion by taking the approximate ground state of (2) to be $\prod_j|+\rangle_j$. The ground state for the case $N=2$ contains $|+\rangle_1|+\rangle_2$ with a (J/Δ)-dependent admixture of $|-\rangle_1|-\rangle_2$. If we consider