comes possible for $\hbar\omega = 21.5$ eV, an excitation from A to C in Fig. 2 (with the initial state A at the Fermi energy). This is illustrated in the second curve of Fig. 3 for an $\hbar\omega$ slightly below threshold. For smaller $\hbar\omega$ the initial state for the G transition moves to lower energy as shown in the third curve of Fig. 3.

Below $\hbar\omega = 19.5$ eV the Q transition (A to B in Fig. 2) becomes possible as shown in the fourth curve of Fig. 3. As $\hbar\omega$ is decreased further, the energies of initial states for both G and Q transitions decrease. When the Q transition is first allowed, the center of the G peak is ~0.4 eV below the Fermi energy in the nearly-free-electron model. The difference in initial energies for the two transitions increases to ~0.6 eV as $\hbar\omega$ is lowered.

The calculation is based on a value $Q = 1.33(2\pi/a)$. The separation between the peaks can be used to determine the difference $G_{110} - Q$. [This depends on a knowledge of $E(\vec{k})$ for the initial- and final-state bands.] Thus, angle-resolved photoemission can be used both to detect the presence of a CDW and to measure its periodicity.

We have performed a similar analysis for sodium. Since the Fermi energy in sodium is about 1.5 times that in potassium, the G transition (A to C in Fig. 2) occurs for $\hbar\omega = 33.4$ eV in the nearly-free-electron model. The Q transition (A to B in Fig. 2) occurs for $\hbar\omega = 31.4$ eV. The spacing between the two peaks is similar to that in potassium, when a value $Q = 1.35(2\pi/a)$ is assumed for sodium. However, because V_{110} in Na is only ~0.2 eV,[9] and the CDW energy gap V is thought to be about 1.2 eV, the peak height for the G transition may be much smaller than that for the Q transition. This disparity could lead to experimental difficulties.

We have shown that angle-resolved photoemission offers a means to detect the presence of an incommensurate CDW. The crucial idea is that the periodicity $\vec{Q}$ of the CDW permits new transitions compared to those allowed by the periodicity of the crystal. By plotting AREDC's for various incident photon energies, it should be possible to identify any additional transitions and (if present) to determine $\vec{Q}$.

[1]A. W. Overhauser, Phys. Rev. 167, 691 (1968).
[2]A. W. Overhauser, Phys. Rev. B 3, 3173 (1971).
[3]A. W. Overhauser, Adv. Phys. 27, 343 (1978).
[4]No results of a detailed search for the CDW satellite reflections have been published.
[5]A. W. Overhauser, Hyperfine Interact. 4, 786 (1978).
[6]G. A. Boutry and H. Dormaut, Philips Tech. Rev. 30, 225 (1969).
[7]A. W. Overhauser and N. R. Butler, Phys. Rev. B 14, 3371 (1976).
[8]G. D. Mahan, Phys. Rev. B 2, 4334 (1970).
[9]F. S. Ham, Phys. Rev. 128, 82 (1962).

Replica-Symmetry Breaking in Spin-Glass Theories

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(Received 7 August 1978; revised manuscript received 6 September 1978)

The instability which arises in current mean-field theories of spin-glasses is removed, within the replica method, by breaking the symmetry between replicas. For the Sherrington-Kirkpatrick (SK) model the spin-glass order parameter has the expansion $q = t + t^2 + O(t^3)$ $(t = 1 - T/T_c)$, which differs at $O(t^2)$ from that given by SK.

Before substantial progress can be made in understanding any phase transition it is essential to obtain a sound understanding of the appropriate mean-field theory. For the spin-glass phase transition the model of Sherrington and Kirkpatrick[1] (SK) provides a suitable starting point. This is a model of Ising spins coupled by random, infinite-ranged exchange interactions independently distributed with a Gaussian probability density. The disorder is quenched, and so the free energy, rather than the partition function, must be averaged over the bond distribution. SK attempted to solve this model, using the "n-replica method,[2]" by means of which one writes $\ln Z = \lim_{n\to 0}(Z^n - 1)/n$ and recognizes that Z^n is the partition function for n identical replicas of the original system. The bond averages may now be taken at the outset yielding a translationally invariant model of coupled replicas. This may be solved in the thermodynamic limit and the analytic continuation to $n=0$ taken at the end of the calculation.[3]

Unfortunately the solution presented by SK suffers from a number of pathologies. Firstly, the entropy becomes negative at sufficiently low temperatures, an impossible result for Ising spins. Secondly, a certain correlation function develops a negative gap below T_c.[4,5] Furthermore, identical results can be obtained without the use of the replica method[6,7] so that the latter cannot be held solely responsible for these pathologies. These difficulties constitute a long-standing puzzle in the theory of spin-glasses.

In this Letter we take the first step towards the formulation of a sensible mean-field theory for spin-glasses. Within the framework of the replica method we argue that the existence of modes with a negative gap implies that the symmetry between replicas should be broken. The simplest possible symmetry breaking is displayed explicitly and shown to remove the instability near T_c, replacing the negative gap by a zero gap. The order parameter is changed from the SK value at $O((1-T/T_c)^2)$.

We consider an Ising spin-glass in which each spin is coupled to z neighbors, and the bonds are independently distributed with a Gaussian probability density. This is equivalent to the SK model in the limit $z\to\infty$. The Landau-Ginzburg-Wilson effective Hamiltonian density takes the form[5,8,9]

$$H=\frac{r}{4}\sum Q_{\alpha\beta}{}^2+\frac{1}{4}\sum(\nabla Q_{\alpha\beta})^2-\frac{w}{6}\sum Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}-\frac{u}{8}\sum Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\delta}Q_{\delta\alpha}+\frac{x}{4}\sum Q_{\alpha\beta}{}^2Q_{\alpha\gamma}{}^2-\frac{y}{8}\sum Q_{\alpha\beta}{}^4+O(Q^5). \tag{1}$$

The sums over the replica indices are unrestricted except that $Q_{\alpha\beta}=0$ for $\alpha=\beta$. The parameters r and w are[8]

$$r=z^2(T^2/T_c{}^2-1),\quad w=z^3, \tag{2}$$

while the coefficients of the quartic terms are[5]

$$u=z^4=x=3y/2. \tag{3}$$

The Edwards-Anderson order parameter $q=\langle\langle s_i\rangle^2\rangle_c$ ($\langle\cdots\rangle$ is a thermal average, $\langle\cdots\rangle_c$ a configuration average, and $s_i=\pm1$ is the spin at the ith site) is given by

$$q=z(T^2/T_c{}^2)\langle Q_{\alpha\beta}\rangle_{n=0}. \tag{4}$$

Sufficiently close to T_c the terms of $O(Q^5)$ in Eq. (1) are negligible. Indeed, the quartic terms should also be negligible close to T_c, but one of these destabilizes the standard theory, by inducing a negative gap in one of the correlation functions,[5] so we shall retain them here.

The standard approach to mean-field theory is to find a stationary point of Eq. (1) for which $Q_{\alpha\beta}(\vec{r})=Q$, all $\alpha\neq\beta$, giving

$$H_{\mathrm{MF}}=\tfrac{1}{4}n(n-1)\{rQ^2-\tfrac{2}{3}(n-2)wQ^3-\tfrac{1}{2}u(n^2-3n+3)Q^4+x(n-1)Q^4-\tfrac{1}{2}yQ^4\}. \tag{5}$$

The extremum equation $dH_{\mathrm{MF}}/dQ=0$ yields for $n=0$ and $r<0$ a nontrivial root satisfying the equation

$$|r|-2wQ+(y+2x+3u)Q^2=0, \tag{6}$$

where the root which vanishes at $r=0$ is to be selected. In the vicinity of the critical point one obtains

$$Q=|r|/2w+(y+2x+3u)|r|^2/8w^3+O(|r|^3). \tag{7}$$

Use of Eqs. (2)–(4) gives finally

$$q_{\mathrm{SK}}=\frac{1}{2}\frac{T^2}{T_c{}^2}\left(1-\frac{T^2}{T_c{}^2}\right)+\frac{17}{24}\frac{T^2}{T_c{}^2}\left(1-\frac{T^2}{T_c{}^2}\right)^2+O((T_c-T)^3), \tag{8}$$

which is the SK result.

To investigate the stability of this mean-field solution we follow de Almeida and Thouless[4] and Pytte and Rudnick[5] and expand the full Hamiltonian with respect to fluctuations about it. Writing, for $\alpha\neq\beta$,

$Q_{\alpha\beta}(\vec{r}) = Q + R_{\alpha\beta}(\vec{r})$, substituting into Eq. (1), and expanding to $O(R^2)$ one obtains[5]

$$H = H_{\rm MF} + \tfrac{1}{4}\{r - (2n-1)uQ^2 + 2(n+1)xQ^2 - 3yQ^2\}\sum R_{\alpha\beta}^2 + \tfrac{1}{4}\sum(\nabla R_{\alpha\beta})^2 - \tfrac{1}{2}Q\{w + (n-1)uQ - 2xQ\}\sum_{\beta\neq\gamma} R_{\alpha\beta}R_{\alpha\gamma} - \tfrac{1}{4}uQ^2\sum{}' R_{\alpha\beta}R_{\gamma\delta}, \tag{9}$$

where $\sum'$ denotes that all indices are different. There are three distinct correlation functions[5,8]: $G_1(q) = \langle R_{\alpha\beta}(\vec{q})R_{\alpha\beta}(-\vec{q})\rangle$, $G_2(q) = \langle R_{\alpha\beta}(\vec{q})R_{\alpha\gamma}(-\vec{q})\rangle$, $\beta\neq\gamma$, and $G_3(q) = \langle R_{\alpha\beta}(\vec{q})R_{\gamma\delta}(-\vec{q})\rangle$, $\alpha, \beta\neq\gamma, \delta$, where $R_{\alpha\beta}(\vec{q})$ is the Fourier transform of $R_{\alpha\beta}(\vec{r})$. Their values may be computed by treating the final two terms of Eq. (9) as perturbations and summing all orders of perturbation theory via Dyson's equations relating the various G's. Of particular interest is the combination $G_R = G_1 - 2G_2 + G_3$ (the "replicon propagator" of Ref. 8) which has for $n=0$ the value[5]

$$G_R(q) = [q^2 - |r| + 2wQ - (3y + 2x + 3u)Q^2]^{-1} \tag{10}$$

$$= [q^2 - 2yQ^2]^{-1}, \tag{11}$$

where the last line follows from Eq. (6). Hence this mode is gapless within Q^3 theory[8] but develops a negative gap in Q^4 theory since $y > 0$. The system is therefore unstable against long-wavelength fluctuations. Furthermore, Eq. (11) is nonsense physically for $y > 0$ since one can show[5] that

$$G_R(0) = AN^{-1}\sum_{i,j}\langle\langle(\langle s_i s_j\rangle - \langle s_i\rangle\langle s_j\rangle)^2\rangle_c \quad (A > 0),$$

which is necessarily positive.

When faced with this kind of instability one usually concludes that the symmetry must be broken. We therefore propose to break the symmetry between replicas. The simplest way of doing this is to divide the n replicas into two groups, containing m and $n-m$ replicas, respectively, and to regard two replicas as equivalent if they belong to the same group. Mean-field theory then contains three different Q's, namely (we take $\alpha < \beta$),

$$\begin{aligned} Q_{\alpha\beta} &= Q_3, \quad \alpha < \beta \leq m \\ Q_{\alpha\beta} &= Q_2, \quad \alpha \leq m < \beta \\ Q_{\alpha\beta} &= Q_1, \quad m < \alpha < \beta. \end{aligned} \tag{12}$$

When this form is substituted into Eq. (1), and the resulting expression varied with respect to Q_1, Q_2, and Q_3, one obtains for an extremum the equations

$$|r|Q_1 + w\{mQ_2^2 + (n-m-2)Q_1^2\} + yQ_1^3 - 2x\{mQ_1Q_2^2 + (n-m-1)Q_1^3\} + u\{m(m-1)Q_3Q_2^2 + 2m(n-m-1)Q_1Q_2^2 + [(n-m)^2 - 3(n-m) + 3]Q_1^3\} = 0, \tag{13}$$

$$|r|Q_2 + wQ_2\{(m-1)Q_3 + (n-m-1)Q_1\} + yQ_2^3 - xQ_2\{nQ_2^2 + [(m-1)Q_3^2 + (n-m-1)Q_1^2]\} + uQ_2\{(m-1)^2Q_3^2 + (m-1)(n-m-1)Q_1Q_3 + m(n-m)Q_2^2 + (n-m-1)^2Q_1^2\} = 0, \tag{14}$$

and a third equation which may be obtained from Eq. (13) by interchanging Q_1 and Q_3 and replacing m by $n-m$.

It is interesting to look for broken-symmetry solutions within Q^3 theory. Since the propagator G_R is gapless for this case we do not anticipate any. If we set $u = 0 = x = y$, the three stationarity equations are easily solved to give two nontrivial solutions:

$$Q_1 = Q_2 = Q_3 = |r|/(2-n)w \tag{15}$$

and

$$Q_1 = \frac{m}{2m-n}\frac{|r|}{w}, \quad Q_2 = \frac{(m^2 - mn + n)^{1/2}}{2m-n}\frac{|r|}{w}, \quad Q_3 = \frac{m-n}{2m-n}\frac{|r|}{w}. \tag{16}$$

Thus a distinct broken-symmetry solution exists for general m and n but collapses, as anticipated, onto the symmetric solution when $n=0$. Note that we have implicitly assumed that we can analytically continue to $n=0$ *holding m fixed*. This is crucial in what follows. We may now proceed perturbatively by expanding the Q's to lowest order in x, y, and u. Perturbing about the broken-symmetry solution we find, setting $n=0$ finally,

$$Q_i = |r|/2w + (a_i y + 2x + 3u)|r|^2/8w^3 + O(|r|^3), \quad i = 1, 2, 3, \tag{17}$$

where

$$a_1 = 3 - 2/m, \quad a_2 = 3 - 2/m^2, \quad a_3 = 3 + 2/m. \tag{18}$$

The term in y has lifted the degeneracy between the symmetric and broken-symmetry solutions. Note that it is precisely this term which is responsible for the instability in the symmetric theory. In choosing a value for m we are guided by the physical requirement that the order parameter q be unique. According to Eq. (4) this requires that all the Q's be the same, which requires in turn that $m = \infty$. This limit restores the symmetry and gives $Q_1 = Q_2 = Q_3 = Q$ with

$$Q = |r|/2w + (3y + 2x + 3u)|r|^2/8w^3 + O(|r|^3), \tag{19}$$

which differs from Eq. (7) merely by the replacement of y by $3y$. As a consequence of this replacement the expansion for q differs from Eq. (8) by the replacement of $\frac{17}{24}$ by $\frac{7}{8}$. The result is simpler when expressed in terms of $t = 1 - T/T_c$, namely,

$$q = t + t^2 + O(t^3), \tag{20}$$

compared with the SK value $q_{SK} = t + \frac{1}{3}t^2 + O(t^3)$. The result $q > q_{SK}$ agrees qualitatively with the estimates of Thouless, Anderson, and Palmer,[10] based on a mixture of analytic and numerical methods.

We turn next to the problem of the stability of the new solution. For the broken-symmetry case the replicon propagator for general m has the form

$$G_R(q) = [q^2 - |r| + 2wQ_1 - 3(u+y)Q_1^2 + 2x\{mQ_2^2 - (m+1)Q_1^2\}]^{-1}, \tag{21}$$

where the replica labels specifying G_1, G_2, and G_3 have been taken without loss of generality to lie in the range $m+1$ to n and the analytic continuation to $n = 0$ has been made. If one substitutes the values given in Eq. (17) for the Q_i one finds that as $m \to \infty$ the instability in G_R is just removed, to $O(|r|^2)$, and once more a gapless mode is obtained. (Any finite value of m would not remove the instability.) The question arises as to what happens at next order in perturbation theory, i.e., $O(|r|^3)$. To compute Q to $O(|r|^3)$ for the SK model one has to include $O(Q^5)$ terms in Eq. (1). However, if we regard Eq. (1) as defining a model problem we can compute the Q's to one higher order in $|r|$ and obtain for $m = \infty$ the result $G_R(q) = \{q^2 + |r|^3 y^2/4w^4\}^{-1}$. Thus the symmetry breaking has left us with a stable solution. However, there also exist other solutions of the stationarity equations which involve further symmetry breaking (obtained by dividing the replicas into three, four, etc., groups). It is possible, for example, that the broken-symmetry solution involving three groups of replicas might restore the gapless mode to $O(|r|^3)$ and give a "better" free energy. Unfortunately, algebraic complexities have prevented us from carrying out this investigation.

It is interesting to note that in models with a Gaussian distribution of spin lengths, such as the spherical model,[11] the term in y which gives rise to the instability is absent from Eq. (1). In fact, of the quartic terms only that in u is present. This feature persists to all orders in Q, with only terms of the form $\mathrm{Tr}\,Q^l$ appearing. For such a model Pytte and Rudnick have shown[5] that $G_R(q)$ is an exactly gapless mode within mean-field theory. No symmetry breaking is therefore required. This may explain why the replica-symmetric theory gives exact results for the spherical model with long-ranged interactions.[11]

Another question of interest is what happens outside mean-field theory. Elsewhere[8] we have considered Q^3 theory for the short-ranged interaction problem, and concluded that to lowest order in the fluctuations [i.e., at $O(w^2)$] G_R develops an instability. Precisely the same symmetry breaking as that described here was successful there in removing the instability, and, furthermore, restored a gapless mode. As a result of that calculation we concluded that the lower critical dimensionality d^*, below which spin-glass order (i.e., $q \neq 0$) is impossible, is 4, since the perturbation expansion for q breaks down for $d < 4$ due to the appearance of an infrared-divergent integral.

In summary, we have attempted a first step towards a sensible mean-field theory of spin-glasses. Many questions remain unanswered, in particular, the implications of replica-symmetry breaking for calculations which do not use the replica method. As a final point we note that the same techniques may be used for p-dimensional spins (where $p = 3$, for example, corresponds to Heisenberg spins) and are equally successful in eliminating instabilities, both in the long-ranged Q^4 theory[12] and the short-ranged Q^3 theory.[13] In contrast to the Ising limit ($p=1$) G_R acquires a positive gap to $O(|r|^2)$ for $p>1$.

[1]D. Sherrington and S. Kirkpatrick, Phys. Rev. Lett. 35, 1792 (1975).
[2]S. F. Edwards and P. W. Anderson, J. Phys. F 5, 965 (1975).
[3]There is some doubt about the validity of interchanging the limit $n\to 0$ and the thermodynamic limit. See J. L. Van Hemmen and R. G. Palmer (to be published) for a discussion.
[4]J. R. L. de Almeida and D. J. Thouless, J. Phys. A 11, 983 (1978).
[5]E. Pytte and J. Rudnick, to be published.
[6]S.-k. Ma and J. Rudnick, to be published.
[7]C. de Dominicis, to be published.
[8]A. J. Bray and M. A. Moore, to be published.
[9]A. B. Harris, T. C. Lubensky, and J. H. Chen, Phys. Rev. Lett. 36, 415 (1976); J. H. Chen and T. C. Lubensky Phys. Rev. B 16, 2106 (1977).
[10]D. J. Thouless, P. W. Anderson, and R. G. Palmer, Philos. Mag. 35, 593 (1977).
[11]J. M. Kosterlitz, D. J. Thouless, and R. C. Jones, Phys. Rev. Lett. 36, 1217 (1976).
[12]A. J. Bray and M. A. Moore, unpublished.
[13]A. J. Bray and M. A. Moore, to be published.

Origin of Surface Resonance States in Nearly-Free-Electron Metals: Al(001)

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(Received 5 July 1978)

Thin-film energy-band determinations of a surface-state–surface-resonance band in Al(001) are found to account completely for and clarify the new angle-resolved photoemission observations of Gartland and Slagsvold. The transition from a true surface state to a surface resonance is explained in terms of a mechanism in nearly-free-electron metals for the formation of surface resonances in "partial" Bragg-reflection bulk energy gaps.

The first directly observed occupied surface state on any simple nearly-free-electron (NFE) metal was very recently reported by Gartland and Slagsvold[1] using angle-resolved photoemission measurements on the (001) face of aluminum. A dominant surface-sensitive peak was interpreted as emission from a two-dimensional band of surface states. Spectra recorded along the $\overline{\Gamma}$-$\overline{X}$ line in the two-dimensional Brillouin zone yielded an experimental dispersion relation for this peak which is parabolic with an effective mass $m^*=(1.03\pm 0.1)m$. By comparison with the projected bulk band structure[2] along $\overline{\Gamma}$-$\overline{X}$, the experimental band starts in the bulk gap at $\overline{\Gamma}$ and rises up in this gap. At about $\vec{k}_\parallel=(0.5,0)$ (units π/a, where a is the surface lattice parameter) it merges into the continuum region and continues smoothly upward to cut E_F at about $\vec{k}_\parallel=(0.8,0)$. While true surface states can exist only in an absolute bulk band gap, the experimental peak shows no effect due to the closing of the absolute gap at about $\vec{k}_\parallel\sim(0.5,0)$, but persists smoothly into the continuum region and up to E_F. A calculation by Pendry[3] of the angle- and energy-resolved photocurrent also showed no changes in the intensity or peak width when the peak leaves the bulk band gap, in good agreement with experiment. Gartland and Slagsvold, therefore, suggested that the existence of the peak for large values of $k_\parallel$ indicates a transition from a true surface state to a surface resonance. These authors were not able, however, to correlate the observed peak behavior for large $k_\parallel$ with the results of existing surface electronic band calculations[2,4]; however, the measured dispersion relation agrees quite well with the behavior of the surface state found in these calculations for $\vec{k}_\parallel<(0.5,0)$.

In this Letter we present thin-film results for the electronic structure of the aluminum (001) surface which completely account for and clarify the experimentally observed behavior. Using our recently developed film linearized augmented plane-wave (LAPW) method,[5] we have performed non-self-consistent calculations for nine- and thirteen-layer aluminum films. We find a surface-state–surface-resonance band which is in very good agreement with the measured dispersion relation and we theoretically explain the observed transition from a true surface state to a surface resonance in terms of a mechanism (which is particularly transparent) in NFE metals for the formation of a surface resonance in

