vergence was considerably slower than before, but agreed with the previous SF state calculation. M was found to be linear in H_0, at least up to H_{SF}, with a slope slightly less than the virtual-crystal-approximation value. At higher H_0, dM/dH_0 decreases noticeably, becoming greatly reduced as M saturates.

H_{SF} is the field at which E_{SF} crosses below the IF exchange-flip state energy (E_{IF}); the results shown in Fig. 2 agree with the data. For $x \approx 0.55$, E_{SF} becomes equal to, but not less than E_{IF}; hence for $x \lesssim 0.55$, no SF occurs. This leveling off of H_{SF} with dilution is directly attributed to the existence of the "flip" states. Since E_{IF} lies below the AF energy, the H_0 required to bring E_{SF} below the former is greater than for the latter.

The calculated ΔM at H_{SF} in sample F is shown in Fig. 3, in the same manner as for the "exchange flips". Note that the calculated ΔM greatly exceeds the observed one, a result not understood but undoubtedly related to the greater complexity of the SF state than has been considered in this model. Further details of this work, including the temperature dependence of H_{SF} and the "exchange-flips" fields, will be published elsewhere.

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[3]No simple probability arguments can be applied to this case, because of the complexity of the implied conditional probabilities. While in the IF case, nearly all "up" sublattice spins remain "up", it is by no means obvious that the neighbors of an $n = 8$ spin (or any other n) will have $n < 8$ (or other n), and will therefore remain "up". This is especially clear for small dilution.

[4]The Gaussian half-widths δH used are 26 kOe (sample F) and 38 kOe (sample G), and for other samples (now shown) vary as $x(1-x)$ as expected for a strain-induced exchange broadening. If the variation of each exchange coupling were statistically independent then one might expect $\delta H \propto n^{1/2}$. For simplicity we have assumed δH not to depend on n.

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Dynamics of Vector Spin-Glasses

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A description of spin-glass dynamics at low temperatures, based on a "harmonic" theory, is presented. The Hamiltonian is approximated by a quadratic form in the spin deviations from a particular local minimum, and diagonalized. The dynamics is governed by the eigenvalue distribution $\rho(\lambda)$. The validity of this description is supported by computer simulations. These suggest that $\rho(0) \neq 0$ in two and three dimensions, implying a logarithmic decay in time of the spin autocorrelation function at low temperatures.

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The unusual low-temperature properties of spin-glasses are thought to be due to the very large number of metastable states which exist in these systems: the Hamiltonian has many local minima of comparable energy. Within the context of the Sherrington-Kirkpatrick model,[1] whose solution plays the role of a mean-field theory for spin-glasses, the number and properties of these minima may be calculated exactly,[2] but for more realistic models analytical progress is difficult. At low temperatures we will assume that at any instant of time the spin configuration is "close" to that characterizing one of the local minima. Dynamical processes are then of two

types: (i) small fluctuations in the neighborhood of a particular minimum, and (ii) thermally activated transitions from one minimum to another ("barrier hopping"). Until now it has been assumed that the latter processes are primarily responsible for the observed slow decays in spin-glasses. The purpose of this note, however, is to point out that for low temperatures, and not-too-long times, a theory based on small fluctuations provides a quantitatively accurate description of the dynamics of two- and three-dimensional systems, and should be relevant for the interpretation of neutron-scattering, Mössbauer, muon-spin-resonance, and ac susceptibility experiments.

For clarity of presentation we consider explicitly the case of planar spins, the case for which the computer simulations were performed, although the results are readily generalized. The Hamiltonian is

$$H = -\tfrac{1}{2}\sum_{i,j} J_{ij}\cos(\theta_i - \theta_j),$$

where the exchange interactions J_{ij} are random variables which are assumed given. We take the spin dynamics to be described by the Langevin equation

$$d\theta_i/dt = -\partial H/\partial\theta_i + f_i = -\sum_j J_{ij}\sin(\theta_i - \theta_j) + f_i, \quad (1)$$

where the kinetic coefficient has been absorbed into the time scale, and $f_i(t)$ is a white-noise source generated by the coupling of the spins to the "lattice":

$$\langle f_i(t) f_j(t')\rangle = 2T\,\delta_{i,j}\,\delta(t-t'). \quad (2)$$

[The addition of an "inertial" term $I\ddot{\theta}_i$ to the left-hand side of Eq. (1) does not change the long-time behavior, which is our primary interest. The effect of a precessional term for the case of Heisenberg spins is more subtle. For the long-range Sherrington-Kirkpatrick model such a term makes only a quantitative difference in the long-time limit.[3]] In the neighborhood of a particular minimum $\{\theta_i^0\}$ we write $\theta_i = \theta_i^0 + \tilde{\theta}_i$ and linearize Eq. (1) in the $\tilde{\theta}_i$:

$$d\tilde{\theta}_i/dt = -\sum_j A_{ij}\tilde{\theta}_j + f_i,$$

$$A_{ij} = \left(\frac{\partial^2 H}{\partial\theta_i\,\partial\theta_j}\right)_0 = \delta_{i,j}\sum_k J_{ik}\cos(\theta_i^0 - \theta_k^0) - J_{ij}\cos(\theta_i^0 - \theta_j^0).$$

Expanding the $\tilde{\theta}_i$ in terms of the eigenstates of the Hessian matrix $\underline{A}$, $\tilde{\theta}_i = \sum_\lambda \langle i|\lambda\rangle\tilde{\theta}_\lambda$, we obtain

$$d\tilde{\theta}_\lambda/dt = -\lambda\tilde{\theta}_\lambda + f_\lambda,$$

$$\langle f_\lambda(t) f_{\lambda'}(t')\rangle = 2T\,\delta_{\lambda,\lambda'}\,\delta(t-t'),$$

whence

$$\langle\tilde{\theta}_\lambda(t)\tilde{\theta}_{\lambda'}(t')\rangle = \delta_{\lambda,\lambda'}(T/\lambda)\exp(-\lambda|t-t'|). \quad (3)$$

Introducing the average spin autocorrelation function

$$a(t) = N^{-1}\sum_i \langle\cos[\theta_i(t) - \theta_i(0)]\rangle \quad (4)$$

and expanding to second order in the displacements $\tilde{\theta}_i$ gives, valid to lowest order in T,

$$a(t) = 1 - T\int(d\lambda/\lambda)\rho(\lambda)[1-\exp(-\lambda t)], \quad (5)$$

where $\rho(\lambda)$ is the [normalized, $\int d\lambda\,\rho(\lambda) = 1$] eigenvalue distribution of the matrix $\underline{A}$.

In the infinite-time limit, $a(t)$ approaches the constant value $a(\infty) = 1 - T\int(d\lambda/\lambda)\rho(\lambda)$, provided the latter integral exists, which requires $\rho(0) = 0$. If there is a nonzero minimum eigenvalue λ_0, then $a(t)$ approaches the limit $a(\infty)$ exponentially fast, $a(t) - a(\infty) \sim \exp(-\lambda_0 t)$. If, on the other hand, the eigenvalue spectrum extends to zero, with $\rho(\lambda) \propto \lambda^x$ as $\lambda \to 0$, then $a(t) - a(\infty) \sim t^{-x}$ for large t. This type of behavior is found[2] in the long-range Sherrington-Kirkpatrick model, with $x = \frac{1}{2}$. Finally, if $\rho(0) \neq 0$ then for long times Eq. (5) gives

$$a(t) = 1 - T[\rho(0)\ln t + \alpha + O(t^{-1})], \quad (6)$$

where $\alpha = \int(d\lambda/\lambda)[\rho(\lambda) - \rho(0)\exp(-\lambda)]$. This type of logartihmic decay has been observed in Monte Carlo simulations of vector spin-glasses.[4] We will report below numerical evidence which suggests that $\rho(0)$ is indeed nonzero for two- and three-dimensional spin-glasses. Note that Eq. (6) cannot hold for arbitrarily long times since, according to Eq. (4), $a(t)$ is bounded from below by -1. We can overcome this problem by evaluating exactly, within the harmonic theory defined by Eq. (3), the right-hand side of Eq. (4):

$$a(t) = N^{-1}\sum_i \exp\{-T\sum_\lambda \lambda^{-1}|\langle i|\lambda\rangle|^2[1-\exp(-\lambda t)]\}.$$

Neglecting the i dependence of $|\langle i|\lambda\rangle|$ (i.e., setting $|\langle i|\lambda\rangle| = 1/\sqrt{N}$, would give $a(t) \simeq \text{const}\; t^{-\rho(0)T}$, a simple exponentiation of Eq. (6). The physical origin of this slow decay is the existence of arbitrarily small eigenvalues of the matrix $\underline{A}$, and the small "restoring force" associated with displacements in the corresponding eigenvector directions.

To investigate the validity of the harmonic theory we have performed computer simulations, based on Eq. (1), for planar spins on square and simple-cubic lattices. Nearest-neighbor interactions J_{ij} were assigned from a Gaussian distribution of zero mean and unit variance. The time t was discretized in units of $\Delta = 0.05$, $t = n\Delta$, and Eqs. (1) and (2) written

$$\theta_i(n+1) = \theta_i(n) - \Delta \sum_j J_{ij} \sin[\theta_i(n) - \theta_j(n)] + f_i'(n), \quad (7)$$

$$\langle f_i'(n) f_j'(m) \rangle = 2\Delta T \, \delta_{i,j} \, \delta_{n,m}. \quad (8)$$

Equation (7) was simply iterated to obtain the orientations at time $(n+1)\Delta$ from those at time $n\Delta$. The noise terms $f_i'(n)$ were taken to be independent random variables drawn from a Gaussian distribution of zero mean and variance $2\Delta T$. The initial spin orientations were chosen to be independent random variables uniformly distributed between 0 and 2π. For some simulations (particularly those at lower temperatures) the system was first "quenched" to zero temperature by successively aligning spins with their local fields until the energy per spin decreased by less than a specified amount (usually 10^{-11}) after a further ten scans through the system. Before starting to monitor the spin orientations, Eq. (7) was first iterated 2000 times (corresponding to 100 real time units) in order to allow the system to attain equilibrium at the given temperature.

Following Binder and co-workers[4,5] we did not directly compute the autocorrelation function $a(t)$ since this tends to be very noisy. Instead we computed the Edwards-Anderson order parameter $q(t) = N^{-1} \sum_i \langle \vec{S}_i \rangle_t^2$, where $\langle \cdots \rangle_t$ indicates a time average. In discretized time,

$$q(n) = (Nn^2)^{-1} \sum_i \sum_{r=1}^{n} \sum_{s=1}^{n} \cos[\theta_i(r) - \theta_i(s)]. \quad (9)$$

If we assume that the angular fluctuations are indeed small, we can expand to second order in the angular deviations $\tilde{\theta}_i$ to obtain

$$q(n) \simeq 1 - (Nn)^{-1} \sum_\lambda \sum_r \tilde{\theta}_\lambda^2(r) + (Nn^2)^{-1} \sum_\lambda \sum_{r,s} \tilde{\theta}_\lambda(r) \tilde{\theta}_\lambda(s). \quad (10)$$

The discrete-time analog of Eq. (4) is

$$\langle \tilde{\theta}_\lambda(r) \tilde{\theta}_{\lambda'}(s) \rangle = \delta_{\lambda,\lambda'} (T/\lambda)(1 - \Delta\lambda)^{|r-s|}. \quad (11)$$

In the thermodynamic limit the fluctuating quantities in Eq. (10) may be replaced by their expectation values, giving

$$q(n) = 1 - (T/Nn^2) \sum_\lambda \{n(n-1) - (2n/\Delta\lambda) a_\lambda + [2a_\lambda/(\Delta\lambda)^2](1 - a_\lambda^n)\} \lambda^{-1} + O(T), \quad (12)$$

where $a_\lambda = 1 - \Delta\lambda$. Results for $q(n)$, computed with use of Eq. (9), are presented in Fig. 1 in the form $(1-q)/T$ vs $\ln t$, where $t = n\Delta$, for a 40×40 system and a $10 \times 10 \times 10$ system, at various temperatures T. Equation (12) suggests that, for T sufficiently small, $(1-q)/T$ should be a function of n only. This is borne out by the data, especially in the two-dimensional case: The data at different temperatures lie almost on a universal curve. The small systematic variations with temperature evident in the three-dimensional data presumably reflect the leading corrections to the harmonic approximation and/or the effect of higher-order terms in the expansion of the cosine omitted from Eq. (10), or even the effects of barrier hopping. All these effects will be more important at higher temperatures. It is not clear why the deviations are more pronounced in three dimensions than in two. The breaking away of the data from the universal curve at long times, which is apparent in the higher-temperature data, is easily understood: since $q \geq 0$ by definition, the function $(1-q)/T$ is bounded above by $1/T$, a temperature-dependent upper limit.

To obtain an independent estimate for the limiting universal curves we have evaluated numerically the right-hand side of Eq. (12) by the following device. Starting from a particular metastable state, the system was randomized by adding to each angle θ_i a small fluctuation $\tilde{\theta}_i(0)$ generated from a symmetric probability distribution with variance B^2 (the results should be independent, in the thermodynamic limit, of the particular distribution used; we used both "top hat" and Gaussian distributions). The system was then allowed to relax in a deterministic fashion by use of Eq. (7) with no random noise, i.e., at $T = 0$. The spin deviations $\tilde{\theta}_i(n)$ were continuously monitored and the correlation function

$$C(n) = N^{-1} \sum_i \tilde{\theta}_i(n) \tilde{\theta}_i(0)$$

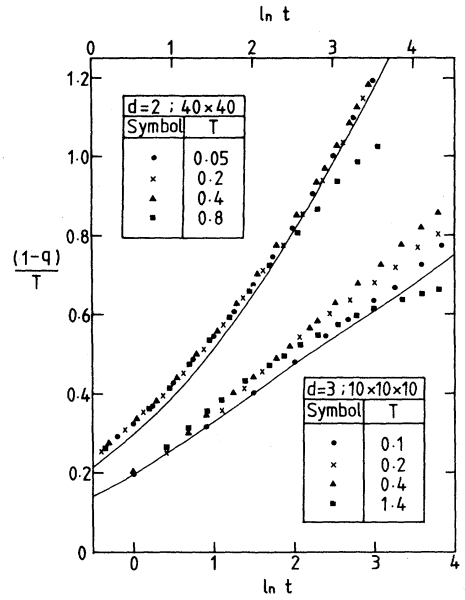

FIG. 1. Dependence of the Edwards-Anderson order parameter q, computed with use of Eq. (9), on time t and temperature T for planar spins in two (upper data) and three (lower data) dimensions. The continuous curves represent the prediction of the "harmonic" theory and were computed with use of Eq. (13). The upper (lower) abscissa refers to the two- (three-) dimensional data.

computed. In terms of the eigenvector amplitudes $\tilde{\theta}_\lambda$,

$$C(n) = N^{-1}\sum_\lambda \tilde{\theta}_\lambda(n)\,\tilde{\theta}_\lambda(0)$$
$$= N^{-1}\sum_\lambda [\tilde{\theta}_\lambda(0)]^2(1-\Delta\lambda)^n,$$

which follows from Eq. (7) with the noise omitted. In the thermodynamic limit we can replace $[\tilde{\theta}_\lambda(0)]^2$ by its mean B^2 to obtain the normalized correlation function

$$\hat{C}(n) = C(n)/C(0) = N^{-1}\sum_\lambda (1-\Delta\lambda)^n.$$

The following result is now readily established:

$$[1-q(n)]/T = (2\Delta/n^2)\sum_{m=1}^{n=1}\sum_{r=1}^{m}\sum_{s=0}^{r-1}\hat{C}(S). \qquad (13)$$

This is shown by explicitly evaluating the triple sum and comparing the result with Eq. (12). Equation (13) establishes a connection between the function $q(n)$, which describes the spin correlations in thermal equilibrium, and the function $\hat{C}(n)$, which describes the nonequilibrium relaxation of the spin fluctuations at zero temperature, both calculated within the harmonic approximation. This approximation should be valid for the calculation of $\hat{C}(n)$, provided that we take B sufficiently small. The simulations for $\hat{C}(n)$ show no significant variations with B for $0.003 < B < 0.1$, and the results should therefore accurately reflect the harmonic theory. The functions obtained by computing the right-hand side of Eq. (13) are shown, for two and three dimensions, by the continuous curves in Fig. 1. These are the desired "universal curves" predicted by the harmonic theory. They provide a quantitative description of the data over a surprisingly large range of temperature. It should be pointed out that these curves do vary somewhat with the random numbers generated for the initial angular variations $\tilde{\theta}_i(0)$—the curves presented in Fig. 1 are typical.

Since the dynamics at all but the shortest times is governed by the small eigenvalues of the matrix $\underline{A}$, we have tried to determine numerically the behavior of $\rho(\lambda)$ as $\lambda \to 0$. To this end we monitored, during the zero-temperature relaxation process described above, the total energy per spin $E(n)$ as well as the correlation function $C(n)$. If $\rho(\lambda) \sim \rho_0\lambda^x$ as $\lambda \to 0$, it is easy to show that $C(n) \sim B^2\rho_0/(n\Delta)^{1+x}$ and $E(n) \sim E_0 + \frac{1}{2}B^2\rho_0/(2n\Delta)^{2+x}$, where E_0 is the energy per spin of the particular local minimum considered. Plots of $-\ln C$ and $-\ln(-dE/dn)$ vs $\ln(n\Delta)$ should give straight lines with slope $1+x$, $3+x$, respectively. The intercepts of these plots determine the amplitude ρ_0. Analysis of such plots, including some data from larger systems (50×50 and $14\times14\times14$) (details will be presented elsewhere), leads to $x = 0.0 \pm 0.1$ and $\rho_0 = 0.31 \pm 0.05$ for the square lattice and to $x = 0.1 \pm 0.1$ and $\rho_0 = 0.20 \pm 0.05$ for the simple-cubic lattice. Hence the data are consistent with a constant density of eigenvalues at $\lambda = 0$, although a small-power x cannot be ruled out, particularly in three dimensions.

Independent studies of the spectrum $\rho(\lambda)$ for planar spins have been carried out by Huber *et al.*,[6] by direct diagonalization of the matrix $\underline{A}$, for relatively small systems (24×24 and $8\times8\times8$). The behavior at small λ cannot be reliably determined because of the finite-size effects. However, a computation of the dynamic structure factor suggests that the equations of motion $I\ddot{\theta}_i = -\sum_j A_{ij}\times\tilde{\theta}_j$ have long-wavelength, propagating "spin-wave" solutions with a linear dispersion $\omega = uk$ in both two and three dimensions. This suggests $\rho(0) \neq 0$ in two dimensions, the value of $\rho(0)$ deduced from the "velocity" u being in good agreement with our own estimate. In three dimensions, however, the dispersion relation $\omega = uk$ suggests $\rho(\lambda) \propto \lambda^{1/2}$, provided that the "spin waves" ex-

haust the spectrum. The origin of this discrepancy is unclear at present. Note, however, that a coarse rebinning of the histogram of Huber *et al.*, with use of bins of width unity in λ, yields a smooth density of eigenvalues with $\rho(0) \simeq 0.17$, consistent with our estimate above.

As noted above, $\rho(0) \neq 0$ implies logarithmic decays in time of the spin correlation functions at low temperatures. Such decays have been observed in *Cu*-Mn(5 at.%) by Murani,[7] over several decades in time (10^{-10}–10^{-2} s), by combining results obtained from neutron-scattering experiments with use of the spin-echo technique and results obtained from ac susceptibility measurements.

In conclusion, we note that the Langevin dynamics used here has advantages over the conventional Monte Carlo approach, namely that it directly simulates a realistic equation of motion, and consequently might profitably be used for other spin systems. Possible extensions of the present work include applications to realistic Hamiltonians (e.g., spins coupled via the Ruderman-Kittel-Kasuya-Yosida interaction) and magnetic field effects.

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Excitation-Energy Dependence of Photoluminescence Bandwidth in a-As_2S_3: Observation of the Mobility Gap?

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A new optical system incorporating a fast Ge photodiode has made possible the first measurements at short times of the low-energy side of the photoluminescence spectrum of a-As_2S_3. Two photoluminescence processes are separated by their dependence on excitation energy, E_x. A number of observations suggest that the first step in the high-E_x process is the creation of delocalized excitations. The abrupt onset of this process leads to the intimation that it arises from transitions across the mobility gap.

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Several years ago, Bosch and Shah[1] and Murayama, Ninomiya, Suzuki, and Morigaki[2] suggested that the photoluminescence (PL) from a-As_2S_3 involved two processes. By extending the measurements to lower PL energies, we have been able to clearly separate two processes by their dependence on excitation energy E_x. It appears, as suggested by Murayama, Suzuki, and Ninomiya,[3] that at low E_x the excitation process occurs by transitions from localized ground states to localized excited states. On the other hand, at high E_x, the excitation process seems to involve transitions between extended states. The onset of the new excitation process is very abrupt. This suggests that it may provide a direct observation of the mobility edge, the energy which separates localized and extended states.

Three major difficulties had to be overcome before this experiment could be performed. Previous measurements were restricted to PL energies of greater than ~ 1.1 eV, the cutoff energy of the best infrared photomultipliers. The severity of this problem was not apparent to previous workers for the following reason. The PL in the chalcogenide glasses is extremely broad. Consequently, the distortion introduced by the common practice of plotting intensity per unit wavelength versus energy instead of intensity per unit energy had the illusory effect of shifting the PL spectrum to energies high enough to measure with photomultipliers. For the broad spectrum of As_2S_3 this shift can be as large as 0.3 eV. A sec-