Electron-Spin-Resonance Modes and the Edwards-Anderson Theory of the Spin-Glass State

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It is shown that the ESR modes observed in Cu:Mn alloys can be explained in terms of an Edwards-Anderson–type theory for a spin-glass when an anisotropy energy is included. Unlike other theories, the present one involves the conventional form for this anisotropy, $U_K = K\sin^2\theta$, where θ is the angle the local microscopic magnetization makes with the symmetry rather than equilibrium direction. The present theory is distinguished by a predicted, but as yet unobserved, angular dependence of single-crystal samples with axial symmetry.

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Experimentally,[1,2] it has been found that spin-glasses, below their cusp temperature T_G, exhibit a zero-field ESR signal. For small magnetic fields, the resonance condition is given by the linear relationship

$$\omega = \gamma(aH_0 + H_c), \tag{1}$$

where H_0 is the applied static field and the constant $a \lesssim 1$. For zero-field–cooled samples $a \simeq \frac{1}{2}$ while for those cooled in a large field $a \simeq 1$. The additional field H_c is a property of the system; it decreases with increasing temperature going to zero at or about T_G.

The original measurements, by Owen *et al.*,[3] on Cu:Mn were consistent with the resonance condition

$$\omega^2 = \gamma^2(H_0^2 + H_c^2). \tag{2}$$

This formula corresponds to an antiferromagnet with the applied field perpendicular to the sublattice magnetization.[4]

The fact that low-field experiments correspond to (1) rather than (2) has led Saslow[5] and Schultz *et al.*[1] to propose theories in which H_c arises from an anisotropy energy, $U_K(\theta) = K\sin^2\theta$. However, in both of these theories the anisotropy energy is of an unconventional form. Usually the angle θ is that between the local microscopic magnetization and the crystalline direction corresponding to a symmetry axis. In the above theories this angle is redefined as being (the equivalent of) the angle between the magnetization and its equilibrium direction. While the symmetry axis *is* the equilibrium direction in an antiferromagnet, it is not so for the spin-glass. As was appreciated by Schultz *et al.*,[1] the justification for this form of the anisotropy energy is far from obvious.

The purpose of this Letter is to show that a relatively simple antiferromagnetic *model* for the ESR in a spin-glass follows from the inclusion of the conventional form of the anisotropy energy in an Edwards-Anderson[6]–type theory for a spin-glass. Specifically it is assumed that below T_G each spin sees a frozen local field which is oriented at random and determined by an order parameter q. Further comments upon this assumption are to be found at the end of the communication. In addition it is shown for a cubic system that an ESR signal *will* appear at a field given by the resonance condition (1). However, for a single crystal with axial symmetry, the present theory predicts an angular dependence of the resonance condition which might be used to distinguish between the two proposed forms for the anisotropy energy.

Although the picture is still far from clear, recent measurements have cast considerable light on the origin of the anisotropy energy in Cu:Mn[1,2,7]; it is a function of the magnetic ion concentration and increases very rapidly with the addition of heavy nonmagnetic impurities. Fert and Levy[8] have proposed a three-site Dzyaliskinsky-Moryia mechanism to explain these observations. In the present work, we accept the existence of an anisotropy energy without explaining its origin. Initially we consider axial symmetry, which is simplest, but later the results will be generalized to cubic symmetry more relevant to Cu:Mn.

The importance of zero- or small-field ESR in spin-glasses has perhaps not been fully appreciated. In analogy with conventional antiferromagnets, careful measurements of the H_c can help to determine whether or not a phase transition occurs at T_G. In the paramagnetic phase, well above T_G, anisotropy effects are negligible for Cu:Mn; therefore, in general, $H_c \equiv H_c(T)$

$\equiv H_c(q)$, such that $H_c(q=0)=0$, where q is the Edwards-Anderson (or equivalent)[9] order parameter.

The calculations reported here imply that $H_c{}^2 \propto q$. Hence (zero-field) measurements of H_c amount to a direct measurement of the order parameter q. As with a conventional antiferromagnet, scaling behavior near T_G should arise because of critical fluctuations. On the other hand, in a cluster model,[10] a local H_c would form with the clusters and $H_c(T)$ should vary more or less smoothly through T_G.

Measurements of H_c are important for another reason. Given that ESR detects the zero-wave-vector limit of the spin-wave spectrum, there is a gap of order γH_c in the low-energy spin-wave excitations of a spin-glass. As noted by Walker and Walstedt,[11] this gap has repercussions upon the low-temperature specific heat. The measured gap is quite large, e.g., it is found[1] for 10% CuMn that $H_c \sim \frac{1}{2}K$.

The present calculation, in one sense, is less than complete; while it does yield the correct equations of motion for the macroscopic magnetization, it leaves the key parameter H_c undetermined. Anticipating criticism of such an approach, we have also used standard methods[12] to adapt the Edwards-Anderson[6] microscopic spin-wave theory to three dimensions and ESR. We have diagonalized (a part of) the microscopic Hamiltonian using the Holstein-Primakoff[12] and Bogoliubov[12] transformations. The results of this very lengthy and much less transparent calculation will be reported elsewhere. They are in agreement with those derived here but, being restricted to zero temperature, are less general. This second calculation is used here as a justification for what might otherwise seem an intuitive development and to provide a precise value for H_c.

In the Edwards-Anderson theory,[6] below T_G, each spin tends to align along a randomly oriented but static internal field $\vec{H}_{Ei}=\sum_{j\neq i}\lambda_{ij}\vec{M}_j$, where $\lambda_{ij}=J_{ij}/\gamma^2$. Consider initially a uniaxial crystal and take the z direction as the symmetry axis. The effect of a uniform $U_K=K\sin^2\theta$, for small deviations from equilibrium, will be a disordered effective anisotropy field $\vec{H}_{Ai}$.[13] With a static magnetic field $\vec{H}_0$ in the z direction, the equation of motion for the transverse magnetization $M_i{}^+$ of the ith spin will be

$$dM_i{}^+/dt=-i\gamma\left[(H_0+H_{Ai}{}^z+\sum_{j\neq i}\lambda_{ij}M_j{}^z)M_i{}^+ + M_i{}^z\sum_{j\neq i}\lambda_{ij}M_j{}^+\right]. \tag{3}$$

The spins can be divided into those with $H_{Ei}{}^z$ and $H_{Ai}{}^z$ both positive or negative. The equations of motion for the average transverse magnetizations $M_1{}^+$ and $M_2{}^+$ for these two subsets can be written as follows:

$$dM_1{}^+/dt=-i\gamma[(H_0+\lambda M_2{}^z+H_A)M_1{}^+-\lambda M_1{}^z M_2{}^+]-i\gamma H_E\textstyle\sum_n a_n M_n{}^+, \tag{4a}$$

$$dM_2{}^+/dt=-i\gamma[(H_0+\lambda M_1{}^z-H_A)M_2{}^+-\lambda M_2{}^z M_1{}^+]+i\gamma H_E\textstyle\sum_n a_n M_n{}^+, \tag{4b}$$

where (initially) $H_A{}^z$ is the average of the z component of the effective anisotropy field for a given subset.

The effective exchange constant λ is the average of λ_{ij} taken for spin pairs one of which belongs to each subset. This is automatically negative and is distinct from the simple average of λ_{ij} which is small and here assumed zero.

The coordinates $M_n{}^+$ correspond to the other $\vec{k}\neq 0$ modes of the system. These will typically have associated energies $E_n \sim (J_{ij}{}^2)^{1/2}$ and coupling coefficients $a_n \sim N^{-1/2}$; N is the number of spins. If $H_A=0$ then Eqs. (4) must add and all exchange fields cancel; this explains the different signs of the ill-defined M_n term in Eqs. (4). Notice that, because of the random nature of the spin orientation, for a zero-field-cooled sample, the averages of both the anisotropy and the exchange fields lie along the symmetry axis.

If the M_n terms could be ignored, Eqs. (4) are identical to those for a conventional antiferromagnet. *A priori* this will not be the case if H_A is taken simply to be the average of $H_{Ai}{}^z$; however, H_A and a_n are dependent variables and there will exist a value of $H_A \sim \bar{H}_A$ for which the M_n terms give no net perturbation.[14] In addition to the sketchy proof of this given in footnote 14, this approach is ultimately justified by agreement with the more detailed calculations mentioned above.

The roots of Eqs. (4), dropping the $M_n{}^+$ terms, and with the static field parallel to the easy axis,

are

$$\omega=\gamma\{H_0+\tfrac{1}{2}\lambda(M_1^z+M_2^z)\}\pm\{[\tfrac{1}{2}\lambda(M_1^z+M_2^z)]^2+H_A[H_A+\lambda(M_2^z-M_1^z)]\}^{1/2}. \quad (5)$$

Now $M_1^z+M_2^z=\chi_\parallel H_0+M_R$, where M_R is the residual magnetization and $\chi_\parallel$ the parallel susceptibility. The exchange field $2H_E=\lambda(M_2^z-M_1^z)$ and as usual[4] $\chi_\perp=|\lambda|^{-1}$ can be used to eliminate the molecular-field constant. The result is

$$(\omega/\gamma)=(1-\tfrac{1}{2}\alpha)H_0+\tfrac{1}{2}\lambda M_R\pm[(\tfrac{1}{2}\lambda M_R-\tfrac{1}{2}\alpha H_0)^2+H_c^2]^{1/2}, \quad (6)$$

where $\alpha=\chi_\parallel/\chi_\perp$ and $H_c=(2H_EH_A)^{1/2}$. For low fields $(\alpha/2)H_0<H_c$, if $M_R=0$, and taking the upper sign, this simplifies to

$$\omega=\gamma[(1-\tfrac{1}{2}\alpha)H_0+H_c], \quad (7)$$

the same as (1) with $a=1-\frac{1}{2}\alpha=1-\frac{1}{2}(\chi_\parallel/\chi_\perp)$.

The detailed zero-temperature spin-wave theory gave $H_c^2=(2|J_0|K/S^2)(\langle S_z^2\rangle-\langle S_y^2\rangle)$, where the angular brackets indicate an average for different spins in the equilibrium configuration. For a strictly isotropic spin-glass $\langle S_z^2\rangle-\langle S_y^2\rangle\sim K/|J_0|$, whence $H_c\sim K$. Since both H_A and H_E are expected to be proportional to $q^{1/2}$ it follows that $H_c^2\propto q$, i.e., the zero-field resonance frequency is directly related to the order parameter, assuming of course that such a parameter exists.

It is well known[4] that the root (7) depends upon the angle the field makes with the crystal axes. The general solution reduces to

$$\omega=\gamma[H_c\pm(1-\tfrac{1}{2}\alpha)H_0\cos\varphi] \quad (8)$$

provided $H_0\ll H_c$ and φ, the angle the field makes with the easy axis, is not very close to $\pi/2$. Only if $8H_c^2(2-\alpha)^2\cos^2\varphi<H_0^2$ does one obtain the celebrated roots given by (2). (Notice that the α factors drop out and that there is also a longitudinal mode[4] $\omega/\gamma\simeq H_c$ independent of the field H_0.)

For cubic symmetry, relevant to Cu:Mn and other current ESR experiments, there are three equivalent symmetry axes. If the coordinate axes are chosen to coincide with the crystal axes then it is clear on symmetry grounds alone that the equations of motion for the three components of the magnetization must be equivalent, at least in the absence of an external field. Since the equations of the theory are also linear they are invariant to rotations of the coordinate axes. Thus in the presence of a *small* external static field $\vec{H}_0$ the z axis can be rotated to coincide with the direction of the field, and hence the antiferromagnetic model in general and Eq. (6) in particular are valid for an arbitrary field direction relative to the crystal axes; i.e., for a cubic system the ESR is isotropic. The microscopic spin-wave calculation confirms these conclusions. Given that the anisotropy is of the Dzyaliskinsky-Moryia form[8] the dependence $H_c\propto q^{1/2}$ is still implied. A single-ion anisotropy would imply $H_c\propto q$. In either case H_c is still directly related to the order parameter q.

Equation (6) would appear to explain the observations to date.[1,2] This equation is identical to that derived by Schultz *et al.*[1] on a phenomenological basis using the unconventional form for the anisotropy energy. It corresponds well to their zero-field–cooled experiments with $M_R=0$ and $\alpha=1$, i.e., it is implied that $\chi_\parallel=\chi_\perp$, the result expected for an isotropic spin-glass. As for orders of magnitude, the observed $H_c\sim 3$ kG is much larger than known single-ion anisotropy fields. The observed concentration dependence and magnitude of H_c imply that the multi-ion Dzyaliskinsky-Moryia contribution[8] is of importance. The experiments of Monod and Berthier[2] and some of those of Schultz *et al.*[1] were samples cooled through T_G in a large field $H_{\rm cool}$ (~1–7 kG). In such a case one would expect $\frac{1}{2}\lambda M_R\sim\frac{1}{2}\alpha H_{\rm cool}$, and the condition $(\frac{1}{2}\lambda M_R)^2>H_c^2$ may apply. The interesting root of (6) reduces to

$$\omega=\gamma(H_0+\tilde{H}_c), \quad (9a)$$

$$\tilde{H}_c=H_c^2/\lambda M_R. \quad (9b)$$

The *effective* anisotropy field $\tilde{H}_c\sim 1/M_R$, as observed.[2] Notice that the ratio α has dropped out of (9a); thus the constant a in (1) will be close to unity, also in agreement with experiment.[2] Since $\frac{1}{2}\alpha H$ and $\frac{1}{2}\lambda M_R$ may either add or subtract in (6) this formula is also consistent with the peculiar macroscopic anisotropy[1] relative to the direction of $\vec{M}_R$.

Of course, the key questions which remain to be answered experimentally are whether the dependence $H_c^2\propto q$ can be confirmed, lending support to the hypothesis of a phase transition at T_G, and whether the anisotropy is referred to the crystal or equilibrium direction, i.e., whether the angular dependence predicted by (8) will be observed for single-crystal samples of axial symmetry in small fields. Good candidates

might be Zn:Mn or Mg:Mn.

Finally it is relevant to comment on the time scale of an ESR experiment. The assumption that $\vec{H}_{Ei}$ is not a function of time and therefore that the order parameter q is well defined is not essential to the above derivation. If the average magnitude of $\vec{H}_{Ei}$ over all spins is a constant and if the direction of $\vec{H}_{Ei}$ changes slowly on the time scale of the experiment (say 10^{-9}–10^{-10} sec) then our results are unchanged. Thus ESR can confirm, or not, the existence of an order parameter only upon this rather short time scale.

The author acknowledges informative discussions with Professor M. Hardiman, Professor S. Schultz, and Professor D. R. Fredkin and the hospitality of Professor R. Orbach and his group at the University of California, Los Angeles. Recently K. W. Becker has derived similar results to those given here.[15] There appear, however, to be significant differences between his and the present results.

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[13]Compare $U_K = K\sin^2\theta$ with $U_K = H_A M\cos(\theta+\Omega)$. The latter corresponds to an anisotropy field in the plane of the spin and the z axis but tilted an angle Ω from the z axis, away from the spin. The two potentials will be equivalent, for small deviations from equilibrium, if the first and second derivatives are equal. This requires $-MH_A\sin(\theta+\Omega) = K\sin 2\theta$ and $H_A M\cos(\theta+\Omega) = -2K\cos 2\theta$, which can always be satisfied. It is clear that $H_A(\theta)$ and $\Omega \equiv \Omega(\theta)$; thus even if the K is the same for each spin, H_A and Ω will manifest the disorder of the angles θ.

[14]The demonstration of this depends on the results which follow in the text. The coordinate which corresponds to the solution (6) is $m_+ = M_1^+ + [1+(H_c/H_E)] \times M_2^+$ (for simplicity, with M_R and H_0 zero). The equation of motion for this coordinate is

$$dm_+/dt = \pm\, i\gamma H_c m_+ \pm i\gamma H_c \Sigma_n a_n M_n^+ .$$

The corrections due to the last term are not small: $\Delta\omega/\gamma \sim H_E \times (H_c/H_E)^{n-1} \sim H_c$, which is *not* negligible. However, since this term *is* perturbative one may write $\gamma H_c \Sigma_n a_n M_n^+ \simeq i\gamma(\Delta H_c) m_\pm$ + higher order. Alternatively

$$i\gamma H_E \Sigma_n a_n M_n \simeq i\gamma(\Delta H_c H_E)\{M_1^+ + [1\pm(H_c/H_E)]M_2^+\},$$

which can be included in Eqs. (4) by a renormalization of $H_A \to H_A + \Delta H_A$ plus negligible (since $H_A \ll H_E$) renormalizations of the exchange fields λM_1^z and λM_2^z. This justifies the neglect of the last terms in Eqs. (4). Notice that, since some of the M_n^+ will be degenerate with the uniform mode (since its frequency is shifted up by H_c), this term will also produce a H_c-dependent width.

[15]K. W. Becker, unpublished.