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Electron-spin resonance in insulating doped semiconductors

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Spin dynamics of shallow impurity electrons in the insulating phase of n-doped semiconductors is examined within the framework of the scaling theory of a disordered spin-$\frac{1}{2}$ Heisenberg antiferromagnet. Quantum fluctuations of the donor nuclear spins are included and found to be important in determining the ESR line shape and position. With use of the known hyperfine constant, a quantitative fit to the experimental results is obtained, including the dramatic temperature and frequency dependence of the linewidth and resonance field seen in phosphorus-doped silicon at millikelvin temperatures.

Studies of the donor electrons in uncompensated doped semiconductors as a function of donor concentration (n) have provided a great deal of information[1] on the metal-insulator transition which occurs at a critical value of n ($n = n_c$). At low doping densities ($n \ll n_c$), however, each donor nucleus binds a single electron in a hydrogenic $1s$ state, and the (exponential) overlap between electrons on different donors leads to an antiferromagnetic exchange interaction.[2] The system therefore behaves like a random spin-$\frac{1}{2}$ Heisenberg antiferromagnet and has been modeled as such using numerical cluster diagonalization[3,4] and hierarchical pair schemes.[4,5] A more complete analysis was performed by Bhatt and Lee (BL)[6] using a renormalization method based upon eliminating strongly coupled pairs of spins. This analysis describes the static magnetic properties of the system well at temperatures below 4 K for n up to $0.7n_c$.[3,4,7]

In contrast to static properties, there has been little theoretical understanding of the spin dynamics of these systems, although various experimental attempts have been made.[8–10] In particular, a recent electron-spin-resonance (ESR) study on phosphorus-doped silicon by Murayama, Clark, and Sanny (MCS)[10] while confirming static results, has exhibited unusual behavior in the absorption line shape and position. The linewidth $\Delta H_{1/2}$ of the signal is temperature dependent and increases rapidly as the temperature is lowered. More remarkably, $\Delta H_{1/2}$ is strongly frequency dependent, being much larger at higher frequencies. The resonance field H_0 is also temperature and frequency dependent. This rich variety of phenomena is summarized in Figs. 1(a) and 1(b). The temperature-dependent broadening of the ESR line has also been observed on the metallic side.[11]

Existing theories of electron-spin resonance are inadequate in explaining the phenomena observed.[12,13] The only theory which is valid in the experimental regime of small external fields is that of Kubo and Toyabe.[13] This theory treats the nuclear fields as classical random fields, and as we shall see such a picture is inadequate. In fact, application of this theory to this system does not even give the trends shown in Fig. 1.

The BL scaling scheme for the disordered spin-$\frac{1}{2}$ antiferromagnet starts from the crucial observation that the distribution of the *logarithm* of the largest bond connected to any site has a large width. This follows from the assumption of a random distribution of spin sites and an exponential dependence of the exchange constant upon the distance between two sites. Consequently, as the temperature T is lowered, bonds J larger than T cause pairs of spins to lock into singlets; the only effect of the triplet excitation of this pair of spins will be to renormalize the remaining exchange interactions in the system. Implementing this description as a renormalization scheme on the computer has given a successful picture of the static magnetic properties of P-doped Si. In this paper we show that the dynamic properties of the electrons which are measured in an ESR experiment can also be well described within this renormalization scheme. The calculations below yield a parameterless fit of the complicated behavior of $\Delta H_{1/2}$ and H_0 as a function of frequency and temperature. The insight gained from our analysis is also found to be useful in interpreting recent results for n just above n_c in the metallic phase.[11,14]

The relevant Hamiltonian for the ESR experiment is

$$H = \sum_{i>j} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j + A\sum_i \mathbf{I}_i\cdot\mathbf{S}_i + h\sum_i S_{iz} \ . \qquad (1)$$

The electron spins $\mathbf{S}_i$ interact with each other via an antiferromagnetic exchange and with the phosphorus nuclear spins $\mathbf{I}_i$ via a contact hyperfine interaction A. The electrons also interact with the ^{29}Si nuclei but the magnitude of this interaction is small.[15] The interaction of the external magnetic field h with the nuclear spins is neglected because the nuclear magneton is much smaller than the electron magneton. Magnetic dipole interactions are too small to be of any importance. We have scaled out the electron magneton and Planck's constant. In these units, 117.5 MHz≡42 G≡5.64 mK. The hyperfine constant A is 42 G. In the MCS experiment the external field h was smaller than the internal hyperfine field $A/2$ on each electron and the experiment was performed while scanning h at fixed external frequency ω. These two facts will be of critical importance.

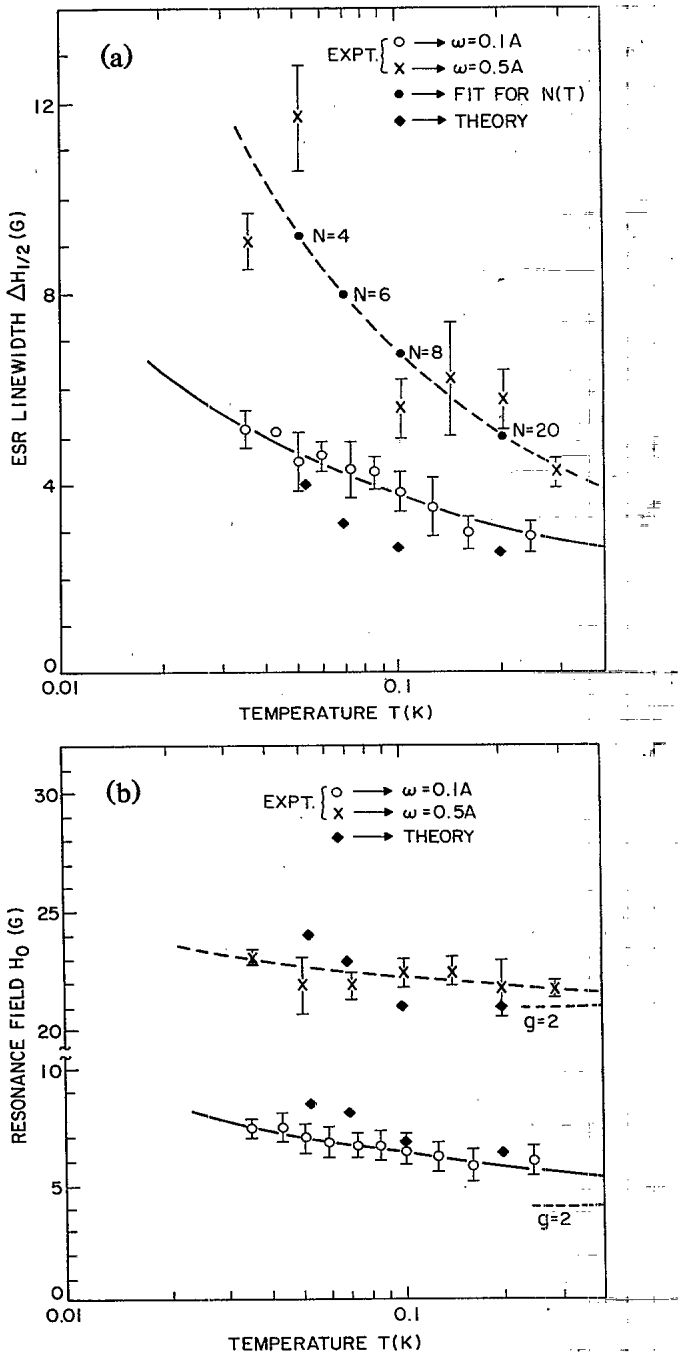

FIG. 1. (a) The linewidth $\Delta H_{1/2}$ and (b) the resonance field H_0 as a function of temperature. The crosses and the dots are experimental measurements of MCS at the frequencies $0.5A$ and $0.1A$. The dashed and dotted lines were drawn through the experimental data by MCS. The circles represent the points used to determine $N(T)$ and the diamonds are the predictions obtained from this $N(T)$.

The approach of this paper is as follows. It is argued that the ESR experiment is sensitive to the diffusion of the electron spin over a time of order T_2^{-1}, during which the electron-spin excitation is concentrated on a cluster of size N. The ESR line shape for such small clusters is determined exactly. Fitting this calculation with the experimental values of $\Delta H_{1/2}$ at a large frequency ($\omega \approx A$) as a function of T yields a cluster size function $N(T)$. The remaining experimental data are now *predicted*. The BL scaling theory is used to obtain an independent determination of $N(T)$ and is compared with that deduced from the experiments.

We begin with a qualitative discussion of the linewidth at very large external frequencies ($\omega \gg A$). At a temperature T, all frozen singlet pairs, with $J > T$, will not contribute to the absorption spectrum. The resonance field H_0 is given by the $g=2$ factor, and the linewidth is determined from motional narrowing considerations. We consider an electron spin hopping from site to site with a frequency given by the exchange constant J between the sites. Let the *total* time a spin spends at a given site within a dephasing time T_2 be τ_c. If the spin visits N sites within a time T_2, the total amount of dephasing is $(\Delta\phi)_N = \sqrt{N} A \tau_c/2 \approx 1$. The $\sqrt{N}$ factor arises from the fact that the sign of the dephasing at each site is random. There are now two regimes of interest. In regime I the spin excitation has a small probability of returning to a given site within a time T_2. This happens in a crystalline antiferromagnet where all the exchange constants are the same. In this case, τ_c is $1/J$ and we get

$$\frac{1}{T_2} = \frac{A^2}{4J}. \tag{2}$$

In regime II, the distribution of exchange constants can be such as to make return of the spin excitation to any site very likely. On its second visit to a site, the electron spin will *not* see a random phase. Now τ_c is T_2/N and

$$\frac{1}{T_2} = \frac{A}{2\sqrt{N}}. \tag{3}$$

We emphasize that in this regime, unlike regime 1, N depends more on the distribution of the exhange constants, rather than their overall magnitude as described below. We claim that it is this regime which is relevant to the MCS experiment.

When the external field is comparable to the internal fields, a more quantitative approach is necessary. Let us assume it is possible, at each temperature T, to divide the system into clusters of a typical size N. An algorithm for doing this is described later. The size of the cluster will be determined by the number of sites the spin can visit in a time T_2. The Hamiltonian for this cluster will be exactly the same as Eq. (1), where the sums are now restricted to

sites of the cluster. Because the near-neighbor bonds are much greater than the hyperfine constant A, it is a good approximation to first diagonalize the exchange part of the Hamiltonian. This will give rise to a set of levels with spin S and degeneracy $2S+1$. Using the Clebsch-Gordon decomposition theorem within each degenerate manifold, we may write $\mathbf{S}_i = \alpha_i \mathbf{S}$ with $\sum_i \alpha_i = 1$. The quantities α_i are numbers which depend upon the configuration of the exchange constants. The projected Hamiltonian H_p within this manifold is therefore

$$H_p = A\mathbf{S}\cdot\left(\sum_i \alpha_i \mathbf{I}_i\right) + hS_z \ . \tag{4}$$

For large external fields, application of the method of moments[12] to H_p, yields a linewidth $\Delta H_{1/2} = A(\sum_i \alpha_i^2)^{1/2}/2 \approx A/2\sqrt{N}$. This is the correct answer for regime II. If we had used the method of moments upon the original Hamiltonian H [Eq. (1)] we would have obtained an answer like that of Eq. (2). The reason the method of moments breaks down for H is that the moment sums are dominated by very weak absorptions, deep in the tail of the spectrum.

For small external fields, an exact solution of H_p is necessary with cluster sizes N ranging from 4 to 20. We choose clusters of a fixed size N from the BL simulation and determine the values of S and α_i. The number α_i can be negative, but the absorption spectrum can be shown to be independent of the sign of α_i. We then calculate the exact absorption spectrum for a fixed external frequency, while scanning the field h. This procedure involves diagonalizing H for each value of the field h. Each absorption line is broadened out to a sharp Gaussian so as to enable us to find the field at which a transition at a given frequency occurs. We average the absorption spectrum over an ensemble of values of S and α_i. We find that using about five different sets of values provides a good average. When N gets greater than 7, complete diagonalization from a random set of α_i is impractical. However, for the special case $\alpha_i = 1/N$ the symmetry of the situation permits quick diagonalization. Experience from smaller clusters shows that restricting to this special set of values of α_i and averaging over different values of S, does not appreciably effect the final answer. Calculated absorption spectra for $N=4$ and 20 are shown in Fig. 2 for external frequencies of $0.1A$ and $0.5A$. The values of $\Delta H_{1/2}$ and H_0 are determined from these spectra by calculating their first and second moments.

It now remains to determine the typical cluster size $N(T)$ for a given temperature T. We do this by fitting the value of $\Delta H_{1/2}$ at $\omega = 0.5A$ to the experimental measurement. Knowing the value of N we are then able to predict, for this temperature, the value of $\Delta H_{1/2}$ at $\omega = 0.1A$ and the values of H_0 at both frequencies. This involves a nontrivial test of the new ideas in this paper because $\Delta H_{1/2}$ at $\omega = 0.5A$ is closest to the "classical" value given by Eq. (3). The other values which are now *predicted* are quite different from the "classical" values.

The results of these predictions are shown by the diamonds in Figs. 1(a) and 1(b). We see that the overall trends are captured rather well. The resonance field H_0 for $\omega = 0.1A$ tends to a value *twice* the classical $g=2$ prediction in both the experiment and the calculation. For the linewidth $\Delta H_{1/2}$, classical theory predicts *no* frequency dependence. The strong decrease in $\Delta H_{1/2}$ with a change in frequency from $0.5A$ to $0.1A$ observed experimentally is well reproduced in this calculation. The remaining discrepancies between our calculation and the experiment are well within the uncertainties in both the theory and the experiment. The systematic difference for $\Delta H_{1/2}$ at $\omega = 0.1A$ is probably due to the small additional broadening from the ^{29}Si nuclei. The important point is, however, that unlike all existing theories, we have reproduced the correct direction and order of magnitude of the frequency and temperature dependence of the linewidth.

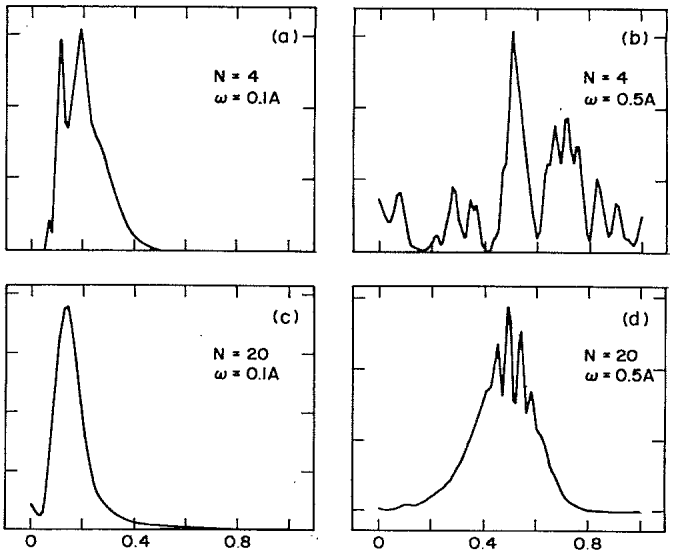

FIG. 2. ESR spectra of small clusters. The x axis is the magnetic field h in units of the hyperfine constant A and the y axis represents intensity in arbitrary units.

We have now shown that the unusual frequency dependence of $\Delta H_{1/2}$ and H_0 arises from the importance of the quantum fluctuations of the nuclear spins for small clusters. Such behavior is absent in the classical models of motional narrowing.[12,13] A simple way of understanding these trends is by examining carefully the absorption spectrum for a *single* electron interacting with a nuclear spin (see Fig. 9 in MCS for the well-known energy-level spectrum). For very small external frequencies one finds $H_0 \approx 2\omega$, which is twice the result for large external frequencies $H_0 = \omega$. An isolated electron spin also has $H_0 = \omega$. The spacing between the two absorption lines, which may be interpreted as $2\Delta H_{1/2}$, is A for large frequencies, but starts decreasing when ω becomes comparable to A, tending 0 at $\omega = 0$. These features capture the trends obtained above as the cluster size becomes small.

In the second part of the calculation, the BL simulation is used to obtain an independent determination of $N(T)$. To dissect the system into clusters, the first step is to remove all bonds that are smaller than $A/2$. (If the spin used these bonds to hop from site to site, it would completely dephase within the time it spent at any site.) While this action is all that is needed for the small clusters ($N < 6$) that are created, there are also a few very large

clusters left behind. If the spin visited every site of this cluster, it could on the average spend only a time T_2/N per site. This implies that every bond which is holding the cluster together must be larger than N/T_2. Using the value of T_2 above, we require that every bond J holding the cluster together satisfy $J > A/2\sqrt{N}$. This requirement is implemented by growing clusters from a site by picking bonds at random. To optimize the growth process, bonds which are well above the lower bound are always kept, while those which barely satisfy it are kept only with a small probability. While this procedure is certainly not rigorous, we expect it to work well because of the wide logarithmic range over which nearest-neighbor bonds are distributed. The cluster size distribution is found to be insensitive to the precise algorithm chosen to define them. The mean and standard deviation of a simulation at temperature T are compared with the $N(T)$ obtained from the experiment in Table I. The agreement is heartening considering the simplicity of the second part of the calculation. Note that we did not attempt to make a quantitative fit using the complications of the actual dependence of the exchange constant upon the distance between the spins as discussed in Ref. 4.

To conclude, we have shown how ESR can be a powerful probe of the nature of the spin excitations in disordered antiferromagnets. Over the time scales measured by the experiments, the spin excitations are localized on small clusters. This localization is well described within the framework of the BL scaling theory. The localization enhances quantum fluctuations of the nuclei leading to unusual behavior in the ESR spectrum. Similar enhancements of the nuclear spin fluctuations from disorder also appear on the metallic side.[14] ESR studies at millikelvin temperatures have only been done in phosphorus-doped silicon. Experiments in other doped semiconductors will be useful in confirming the ideas presented in this paper.

TABLE I. Comparison of the cluster sizes $N(T)$ obtained from fitting to the experiment with the simulation. SD denotes standard deviation.

	Experiment	Simulation	
T	$N(T)$	Mean	SD
53	4	5.8	2.7
70	6	6.8	4.0
100	8	7.3	3.0
200	20	11.0	6.0

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