

Low-temperature magnetic properties of submetallic phosphorous-doped silicon

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Measurements of the electron-spin-resonance properties of Si:P with dopant concentration of $n = 2.05 \times 10^{18} \text{ cm}^{-3}$ (somewhat below the metal-insulating transition) at low temperatures (0.035 to 4.2 K) and low frequencies (11.5–58.2 MHz) are reported. They show a substantial deviation from Curie-law behavior for the susceptibility, in agreement with previous static experiments. An internal field is observed to develop as the temperature is lowered. At 35 mK, the internal field has a magnitude of 2.1 Oe and is directed opposite to the externally applied field. The buildup of the internal field is accompanied by an increase in the resonance linewidth. Both the linewidth and the internal field can be fitted with a power-law divergence that suggests critical behavior relative to a phase transition at zero temperature. At all temperatures investigated the relaxation time of the magnetization is observed to be less than 1 ms, and is interpreted as relaxation of the Zeeman reservoir to the exchange reservoir.

I. INTRODUCTION

Studies of the metal-insulator ($M-I$) transition in phosphorus-doped silicon¹ (Si:P) and other doped semiconductors have recently focused interest on their low-temperature magnetic properties.² Three of the reasons for this interest are the following: (a) Their magnetic behavior reflects the interactions among the donor or acceptor electrons responsible for their $M-I$ transition, (b) a distinctive type of magnetic behavior (amorphous antiferromagnetism) is observed,²⁻⁴ which reflects the random or disordered nature of these interactions, and (c) the study of this amorphous antiferromagnetism complements research on two other types of random magnetic system—spin-glasses⁵ and the random-exchange Heisenberg antiferromagnetic chain⁶ (REHAC). All three have some properties in common, yet retain essential differences. The main property they all share is a randomness of the interaction among the spins due to their spatial disorder. A further similarity between the spin-glass and the amorphous antiferromagnet is that both are three-dimensional systems and their properties are affected by frustration.^{4,5} On the other hand, they are different, as the microscopic spin-spin interaction in an amorphous antiferromagnet is purely antiferromagnetic, whereas in a spin-glass, the interaction among the spins has both signs, i.e., both ferromagnetic and antiferromagnetic. In comparison with the REHAC, the amorphous antiferromagnet is similar in that both have purely antiferromagnetic exchange, but they are different because the REHAC is one dimensional, whereas the amorphous antiferromagnet is three dimensional. The one dimensionality of the the REHAC means that frustration does not occur to affect its properties. On the other hand, its behavior is strongly governed by renormalization of its exchange interactions.^{6,7}

Recently, there have been two important advances in the understanding of the low-temperature magnetic behavior of Si:P. Experiments on the static magnetic sus-

ceptibility down to a temperature of 10 mK have shown substantial deviations from Curie-law behavior which reflect the random location of the donor spins and their interactions.² In addition, a renormalization calculation has been done which gives a good interpretation of these results.⁸

In this paper, we describe experiments on the low-temperature magnetic properties of P-doped Si at a dopant concentration ($n = 2.05 \times 10^{18} \text{ cm}^{-3}$) slightly below the ($M-I$) transition using low-magnetic-field (4.1–23 Oe) electron-spin resonance down to a temperature of 35 mK. Our work complements and extends previous work on this subject. In comparison to prior ESR measurements on samples near this concentration,⁹⁻¹² they go a factor of about 30 lower in temperature, a factor of about 800 lower in frequency than most of the measurements (9.3 GHz), and a factor of 180 lower in frequency than measurements made¹⁰ at 2 GHz. This latter point is important as it preserves the high-temperature approximation for most of the relevant interactions in the system, even down to 35 mK (see Sec. IV). Although the static measurements² have been carried out to much lower temperatures (2 mK) at relatively low magnetic fields (10–300 Oe), additional features are obtained using ESR methods that were not available in the static methods. These include the internal field that shifts the frequency of the ESR line, as well as the width and shape of the ESR line, which reflect the static and dynamic interactions among the spins. The ESR method also has the advantage of not being sensitive to diamagnetic corrections and the small amounts of surface contamination that occur on the samples.² Further details are presented in Sec. II.

Our experimental results are described in Sec. III. They confirm the non-Curie behavior typical of random systems with moderate-to-strong exchange interactions already seen by static susceptibility measurements.^{2,9,13} In addition, we observed two new effects in the low-temperature ESR properties that are not visible in the pri-

or measurements, and which are a further manifestation of the spin-spin interactions. They are a shift in the field for resonance indicative of an internal field and an order-of-magnitude increase in the ESR linewidth. Both of these effects show a power-law divergence towards $T=0$. Pulsed magnetic field measurements were also used to measure the electron-spin-lattice relaxation time, and determined that it is less than 1 ms over the range of field and temperature investigated.

Although there is an existing interpretation for the susceptibility^{2,8} there is not yet a quantitative theory to explain the internal field and ESR linewidth. The interpretation of the latter results presented in Sec. IV is therefore qualitative and speculative.

II. EXPERIMENTAL DETAILS

The temperature range covered in these experiments is 35 mK to 4 K. Measurements between 35 mK and 1 K were made using a helium dilution refrigerator constructed in our laboratory. The sample was placed in the mixing chamber in direct contact with the mixture. This arrangement insured the best possible thermal contact between the sample and the bath. The working thermometer was a Speer carbon-resistor thermometer which had been calibrated using the nuclear susceptibility and spin-lattice relaxation time of ¹⁹⁵Pt in a finely divided powder of Pt.⁴ We estimate the accuracy of the temperature measurements to be 1 mK or 2%, whichever is greater. Temperatures above 1 K were obtained by placing the sample in the ⁴He bath of a conventional cryostat. We estimate the temperature of these measurements to be accurate to 1%, unless otherwise specified.

Electron-spin-resonance absorption measurements were recorded using a Q -meter circuit¹⁵ which operates at very low excitation levels and whose sensitivity can be accurately calibrated. It can also be operated over the frequency range 0.7–80 MHz. The low-level excitation is important to avoid heating of the sample or saturation of the ESR signal at the low temperatures covered in this work. Because of the sensitivity calibration, it was used to measure the electronic susceptibility χ even when the excitation level was changed to accommodate different temperatures. The wide frequency range permitted investigation of the phenomena over a fairly broad range of applied magnetic field.

The magnetic field (H) was generated by a superconducting solenoid external to the tail of the vacuum can. Because of the low ESR frequency (ω), only rather small values of H were required. Our coil covered ± 300 Oe. It could also be cycled over this range in about 1 ms for use in relaxation-time experiments.

Frequently, the signal-to-noise ratio in these experiments was poor. For this reason, the signal was usually sent to a Nicolet model no. 1072 signal averager and averaged for whatever time was needed to obtain the desired measurement.

The sample used in this work was loaned to us by K. Andres. It has the dimensions $7.0 \times 3.6 \times 3.6$ mm³, and a measured phosphorus concentration $n = 2.05 \times 10^{18}$ cm⁻³. An rf coil was wound directly on the sample for observation of the ESR signals.

III. EXPERIMENTAL RESULTS

In this section we describe the results obtained in our experiments. The basic quantity recorded is the ESR absorption. An example of the signals obtained (after averaging) is shown in Fig. 1, where the signal for two values of ω is shown for two values of the temperature (T). These curves are obtained using direct detection of the spectrometer output level; no field modulation or lock-in detection is employed. The external field is swept symmetrically through zero using a triangular waveform, so that the absorption is seen twice, once at positive field, and once at negative field. The recorded signal is the average of sweeps in both directions. By using a triangular waveform instead of a sawtooth waveform, better averaging of slow drifts in the baseline is achieved. When the width of the absorption is not small compared to the resonance field, there is a substantial overlap of the signals near $H=0$. In this case empirical decomposition into two resonances is used. An example of this kind of decomposition is shown by the dashed lines in the top trace of Fig. 1.

Two of the main experimental results of this work are visible in Fig. 1. Consider, for example, the two upper curves, which correspond to $\omega/2\pi = 11.5$ MHz. There, it is seen that the field for resonance (H_0) at the lower tem-

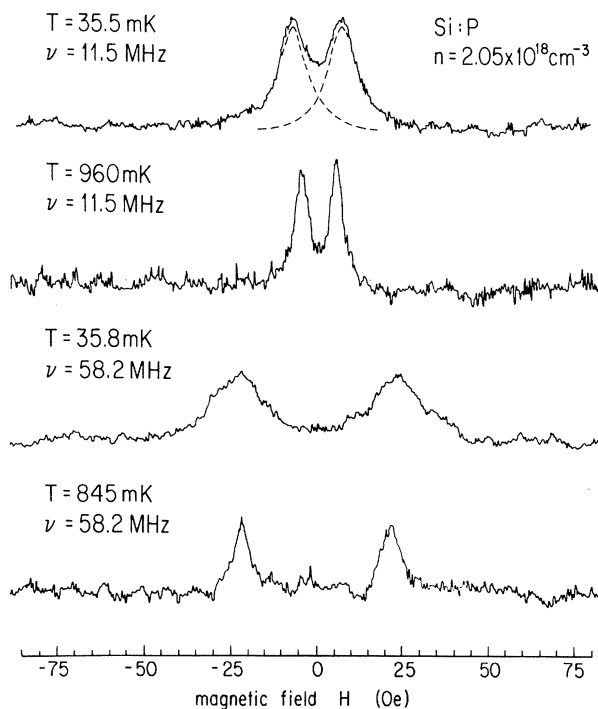


FIG. 1. Electron-spin-resonance absorption signal of Si:P doped to $n = 2.05 \times 10^{18}$ cm⁻³ as a function of applied magnetic field for two values of the resonance frequency and the temperature. The dashed line of the top curve indicates an empirical decomposition of the composite line into its two components. The high-temperature traces show a field for resonance that is higher than that observed at low temperature. This difference indicates the appearance of an internal field at low temperatures which is directed in opposition to the applied field.

perature is larger than that at the higher temperature. This means that as the temperature is decreased, an internal field develops whose direction opposes that of H_0 . The lower two curves show that the same phenomenon is present for a value of ω about 5 times larger. Figure 1 also shows that the ESR linewidth increases with decreasing temperature.

The variation of H_0 with ω at 35 mK is indicated in Fig. 2. A straight line corresponding to the $g=2.00$ of the donor resonance¹⁶ in Si is shown by the solid line. Its extrapolation to $\omega=0$ indicates that at 35 mK there is an internal field $H_i=(2.2\pm 0.1)$ Oe in this sample. The sign of H_i is such that it opposes H . It is also worth noting that H_i tracks H (in opposition) even when H changes sign upon passing through zero. Evidence for this is discussed in more detail below.

The overall variation of H_0 with temperature at two values of ω is shown in Fig. 3. The solid and dashed lines are a guide to the eye. The value of H_i is the increase of H_0 over the free-electron value indicated by the arrow labeled $g=2$. A clear increase in H_i with decreasing T is seen. Our quantitative estimates from Fig. 3 are that the decrease in H_i between 35 mK and 2 K (δH_i) at 58.2 MHz is $\delta H_i=(1.9\pm 0.4)$ Oe and is $\delta H_i=(2.5\pm 0.6)$ Oe at 11.5 MHz. Figure 3 suggests that H_i is nearly zero above 2 K in this sample. If we assume this to be so, it follows that for the range of ω and T covered in this work (and our experimental uncertainties), $\delta H=H_i$, and both are independent of ω . There is some suggestion in Figs. 2 and 3 of a deviation from these conditions at the upper frequency end, but with our experimental uncertainties, it is difficult to tell if such an effect is real. More work at lower T and higher ω is needed to decide this question.

Figure 4 presents the ESR half-width at half-maximum

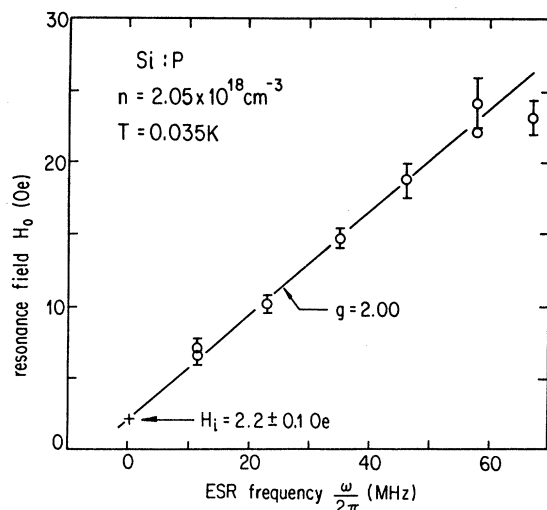


FIG. 2. Field for resonance in Si:P doped to $n=2.05\times 10^{18}$ cm^{-3} as a function of the ESR frequency at $T=35$ mK. The $g=2.00$ slope indicated by the solid line is that expected of noninteracting donors in Si. The intersection at $\omega/2\pi=0$ indicates the presence of a local field directed opposite to the applied field. This local field is interpreted as due to interactions among the donor spins.

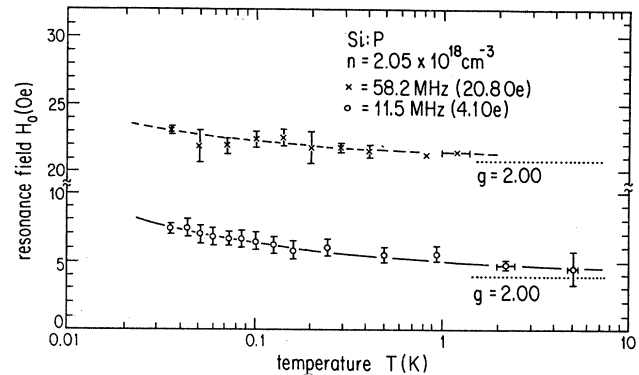


FIG. 3. Field for resonance in Si:P doped to $n=2.05\times 10^{18}$ cm^{-3} as a function of temperature for two resonance frequencies. The solid and dashed lines are a guide to the eye. The increase in H_0 with decreasing temperature indicates the temperature dependence of the local field.

linewidth ($\Delta H_{1/2}$) as a function of T for two values of ω . The solid and dashed lines are a guide to the eye. It is seen that $\Delta H_{1/2}$ increases rapidly with decreasing T . Although this behavior is qualitatively similar to that of H_i , there are two important quantitative differences. The observed variation in $\Delta H_{1/2}$ is larger than that of H_i , and there is a large dependence of $\Delta H_{1/2}$ on ω .

There is independent evidence that the effects just described are properties of the sample, and not artifacts of the apparatus or the way the experiments were done. The first evidence is that on the same run as that used for the Si:P measurements, identical measurements were made on a sample of undoped *trans*-(CH)_x using the same spectrometer, similar operating frequencies, similar power settings, and similar settings of the dilution refrigerator. The *trans*-(CH)_x sample had a similar coil wound about it and was located in the same orientation about 3 mm away from the Si:P sample. Under these conditions, the applied field at one sample was the same as at the other. Since the *trans*-(CH)_x sample showed a $g=2$ resonance and a temperature-independent linewidth over the entire tem-

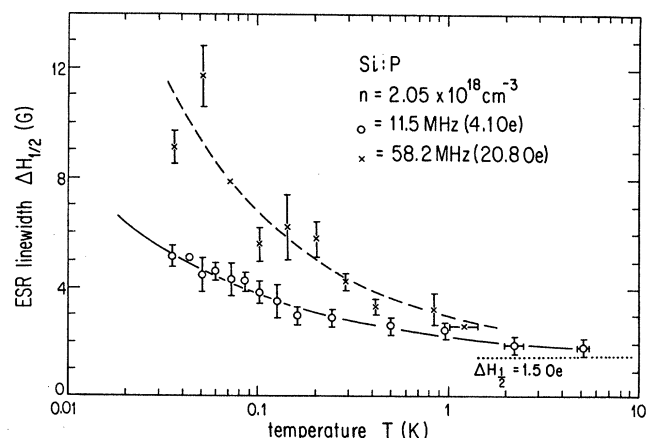


FIG. 4. Electron-spin-resonance linewidth in Si:P doped to $n=2.05\times 10^{18}$ cm^{-3} as a function of temperature for two resonance frequencies. The lines are a guide to the eye.

perature range 0.035–4.2 K, we interpret the changes that occur for Si:P as characteristics of the sample. We also point out that in using the same apparatus for hundreds of comparable measurements of much narrower $g=2$ resonances over many different runs, a limit of spurious or inhomogeneous fields has been established that is orders of magnitude smaller than the effects seen in our Si:P experiments.

It can also be shown that the rf magnetic field used in our experiments is small enough to have a negligible effect upon the results. Although its amplitude is not known exactly, it can be estimated to order of magnitude on the following basis. The rf voltage on the ESR coil was approximately 0.3 mV. From the geometry of the coil, a rough calculation shows that this corresponds to a rf field of about 0.3 mOe. Estimates of this type have been verified with our apparatus in other experiments by using pulsed NMR to calibrate the amplitude of the rf magnetic field. Thus, the rf magnetic field is much smaller than either the field shift or linewidth observed in our experiments. It is also easily shown to be too small to cause appreciable saturation of the resonance signal given the short spin-lattice relaxation time reported at the end of this section.

The absorption line shape is shown in Fig. 5, where the inverse of the intensity $[I(H)]$ normalized to the maximum value $[I(H_0)]$ is plotted as a function of $[(H-H_0)/\Delta H_{1/2}]^2$ for values of ω and T representative of our experiments. It is evident that the measured shapes follow that of a Lorentzian (solid line),

$$I(H_0)/I(H) = 1 + [(H - H_0)/\Delta H_{1/2}]^2. \quad (1)$$

For comparison, a Gaussian shape is indicated by the dashed line.

In addition to showing that the line shape is Lorentzian, we believe that Fig. 5 indicates that there is no hysteresis in the way H_i follows H . If hysteresis were present, it would lead to a composite line shape that is the superposition of the two intrinsic line shapes separated by the hysteresis in H_i . This condition applies because each recording is the average of equal numbers of field sweeps in opposite directions. A large hysteresis would then give two distinct lines in place of one, in clear contradiction to what is seen. It is possible, however, for a small hysteresis simply to broaden the absorption line shape. However, if the intrinsic lines were Lorentzian, the superposition of the two would not be. We have analyzed this case to see how large the hysteresis could be and still give our observed line shapes, and find it to be less than 3% of $\Delta H_{1/2}$. We therefore conclude that Fig. 5 represents the intrinsic line shapes for our samples. It then follows that there is negligible hysteresis and that the values of $\Delta H_{1/2}$ in Fig. 4 are also intrinsic. (These conclusions rest on the reasonable assumption that we are not dealing with two shifted, non-Lorentzian line shapes whose superposition is a single Lorentzian.)

Our experimental results for the magnetic susceptibility are shown in Fig. 6. There, the ESR measurement of χ as a function of T is given for the two frequencies $\omega/2\pi = 11.5$ and 58.2 MHz. These curves are obtained by integrating the area under the ESR absorption line. Since there was no standard available in these experiments to

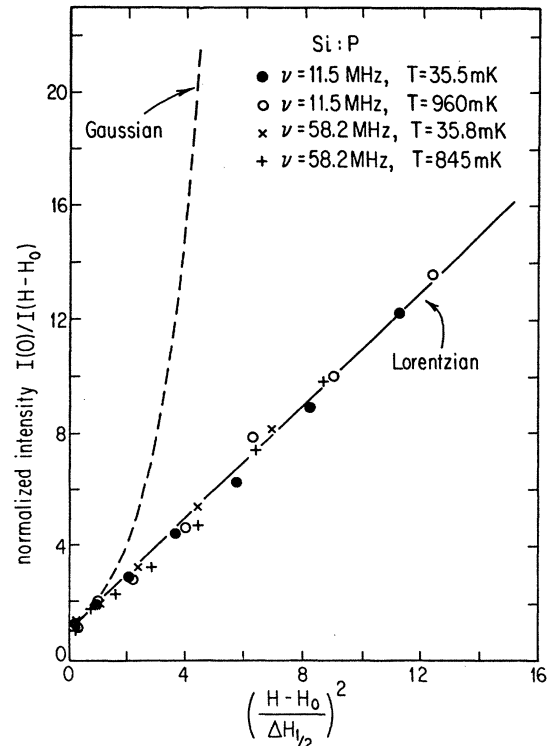


FIG. 5. Normalized line shape of the ESR absorption in Si:P doped to $n = 2.05 \times 10^{18} \text{ cm}^{-3}$ for two frequencies and two temperatures. The solid line corresponds to a Lorentzian shape [Eq. (1)] and the dashed line represents a Gaussian. The close agreement to the Lorentzian form is an indication that hysteresis in the cycling of the local field is negligible, and that the line shape is determined by exchange and/or motional narrowing.

permit an absolute calibration of χ , only the temperature dependence from the relative values are shown. Typical experimental errors in this measurement are indicated by the error flags. The Curie-law behavior, which is charac-

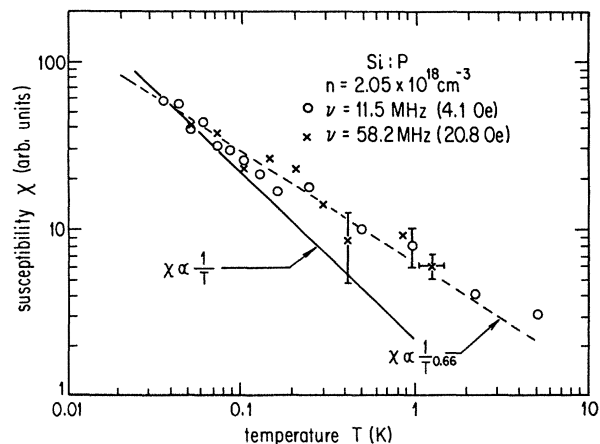


FIG. 6. Temperature dependence of the susceptibility of a sample of Si:P doped to $n = 2.05 \times 10^{18} \text{ cm}^{-3}$ at two different ESR frequencies. The data from the two different frequencies are both displayed on an arbitrary susceptibility scale. The substantial deviation from the Curie-law behavior indicated by the solid line is attributed to the interactions among the spins, and the dashed line indicates the static measurements reported in Ref. 5.

teristic of noninteracting spins, is shown by the solid line. In each figure it is clear that the spin-spin interactions give significant deviations from the Curie law. Comparison of the two figures shows that these deviations are the same for the two values of ω .

Finally, we report an attempt to measure the electronic spin-lattice relaxation time (T_{1e}) on the sample used in this work. The method used is to let the polarization build up at a high field, and then switch rapidly to H_0 and record the subsequent time-dependent behavior of the amplitude of the ESR signal. Even though the field-switching time was about 1 ms, no relaxation was observed, which puts a limit of less than 1 ms on T_{1e} . This limit applies for both frequencies used and over all of the temperature range investigated.

IV. INTERPRETATION

Before presenting the interpretation of our experiments we point out which of the relevant energies in our system are large and which are small compared to the thermal energy kT . At the concentration used in our work, the calculations of Bhatt and Lee⁸ show that over 90% of the donor-exchange couplings exceed 5 K. Thus, our experiments are in the low-temperature regime as far as the donor-exchange energy is concerned. They are, however, in the high-temperature limit for all of the other relevant interactions. These are, respectively, the electronic Zeeman interaction (0.5 and 3 mK for 11.5 and 58.2 Oe), the hyperfine interaction between the donor and the ³¹P nucleus¹⁷ (21 Oe, or 3 mK), the hyperfine interaction with surrounding ²⁹Si nuclei¹⁶ (typically 0.3 mK), the dipolar interaction between bound donors² (typically $\sim 1 \mu\text{K}$), and the Zeeman interaction of the ²⁹Si and ³¹P nuclei ($\leq 2 \mu\text{K}$). Implicit use of these conditions will often be made in the interpretation which follows.

A. Magnetic susceptibility

Since our magnetic susceptibility measurements shown in Fig. 6 are relative measurements, we discuss their temperature dependence only. The main feature they display is a non-Curie behavior at low temperatures. This type of behavior has already been observed at the high-temperature end from microwave ESR measurements^{9,10,12} and from very low to high temperatures using static methods.^{2,13} The ESR measurements were obtained at magnetic fields much larger than those used in our work. The very-low-temperature static measurements² were done at fields (10–300 Oe) similar to those used in our work (4 and 20.8 Oe), whereas the higher-temperature¹³ ones were done at much higher fields. Because the main overlap with our work is the very-low-temperature static measurements,² our discussion centers on a comparison with them.

The low-temperature region of Fig. 6 is fitted reasonably well by the power law $\chi = CT^{-0.66}$, as indicated by the dashed line (C is an undetermined constant). Both values of the applied field give the same result. The observed power-law divergence is an indication that the system is not headed towards a phase transition at a tempera-

ture above $T=0$, as pointed out in earlier work.² This power-law behavior is the same as that reported by Andres *et al.*,² except that our data suggest a slight positive curvature on Fig. 6, whereas theirs has a slight negative curvature on the same kind of graph. The experimental accuracy of our measurements is not sufficiently good to see if this is a real difference, and so we conclude that in the region of overlap, both measurements are in agreement. The work of Andres *et al.* also showed a surprising saturation of the susceptibility below 30 mK that was inaccessible to our experimental setup, so that a confirmation of that behavior was not possible in our work. There was, however, one difference between the two sets of measurement that indicate this question should be pursued further. They indicated a long spin relaxation time that could be interpreted as a problem of thermal contact. We did not observe this long component in our relaxation-time measurements down to the lowest temperatures covered in our work. This may indicate a stronger thermal contact to our sample, which was in direct contact with the helium in the mixing chamber of our refrigerator.

The idea that exchange is important for the interpretation of the low-temperature susceptibility of Si:P at donor concentrations below the $M-I$ transition was proposed a long time ago.^{18,21} We believe the best available interpretation for the power-law behavior shown in Fig. 6 is the three-dimensional (3D) random exchange model used by Andres *et al.*² and advanced further in the scaling studies reported by Bhatt and Lee.⁸ The physical model used in these treatments is one of localized spins, located at random, which have a random antiferromagnetic interaction among the donor spin pairs which is determined by their random separations. Its prediction for χ is approximately a power-law dependence on T , with a donor-concentration-dependent exponent which is on the order of 0.7 for the concentration used in our experiments. This type of model has provided an excellent fit to the low-temperature susceptibility of both Si:P and CdS at donor concentrations below the $M-I$ transition.^{2,6,3} Although the cluster approach of Marko and Quirt¹⁸ has a similar physical content, it has not been developed into a successful set of predictions for the low-temperature behavior of χ . In particular, it indicates a Curie-Weiss behavior at high temperatures and a small deviation in the correct direction at lower temperatures that is not sufficiently well delineated to be useful in the very-low-temperature range.

The success of the random exchange model^{2,8} in explaining the low-temperature behavior of χ is a strong argument for discarding an earlier analysis of experimental results based upon a superposition of a Curie (localized spin population) and a Pauli term (delocalized spin population).¹⁰ At the time these interpretations were made, the true power-law behavior displayed by χ at low temperatures was not yet known.

There is one uncertainty regarding the 3D random exchange model. It is based upon the notion that all of the spins are well localized. On the other hand, it has been proposed from the behavior of the electronic g value in submetallic Si:P that a substantial fraction of the electrons

responsible for χ are delocalized to some extent.¹¹ This situation is similar to that of band ferromagnets, where some of the properties are those of delocalized electrons and others associated with localized electrons. The resolution of this problem for Si:P will require further work, perhaps along the lines of incorporating correlation effects into the description of whatever part of the electron population is delocalized, as well as further experiments on the g shift at very low temperatures, where thermally activated hopping motion is stopped.

B. ESR linewidth and line shape

Another important feature which emerges from our experiments is the large increase in the ESR linewidth with decreasing temperature (Fig. 4). Unlike δH_i , which is nearly independent of H_0 (Figs. 2 and 3), $\Delta H_{1/2}$ has a substantial dependence on it (Fig. 4). This dependence is plotted differently in Fig. 7, where the additional linewidth appearing at lower temperature is shown as a function of temperature on a double-logarithmic plot. The additional linewidth (ΔH_a) is defined as the observed $\Delta H_{1/2} - 1.5$ Oe, where 1.5 Oe is taken as an "intrinsic" linewidth approached near 15 K. What is seen is that ΔH_a exhibits a reasonably well-defined power-law divergence¹⁹ below about 1 K. This behavior is most evident in the 11.5-MHz data, where the smaller linewidth permitted better resolution. Figure 7 also shows that ΔH_a increases by about a factor of 2 when the external field is varied from 4.1 to 20.8 Oe.

The beginning of this increase in $\Delta H_{1/2}$ with decreasing temperature has already been reported in prior work on Si:P by Quirt and Marko,⁹ Maekawa and Kinoshita,¹² and Ue and Maekawa.¹⁰ In all of these cases, the same qualitative behavior seen in our measurements was reported, but the temperature was not lowered enough to show the large variation that actually occurs. In addition, all of the earlier measurements were made in the presence of much

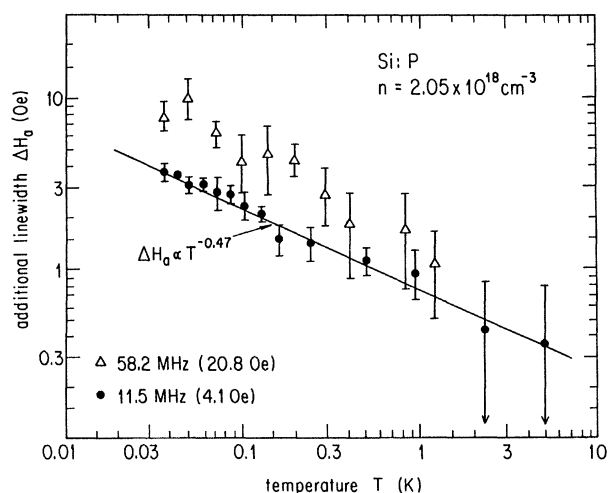


FIG. 7. Additional linewidth of Si:P doped to $n = 2.05 \times 10^{18}$ cm^{-3} as a function of temperature at two values of the magnetic field. The solid line is a guide to the eye. It suggests a critical behavior at $T = 0$.

higher applied fields.

The Lorentzian line shape recorded in our experiments (Fig. 5) is in agreement with those reported in earlier work¹¹ for this concentration range. The point that is new with our work is that it persists to much lower temperatures and occurs for a very low applied field.

We now comment on the physical implications and interpretation of the linewidth and line shape observed in our measurements. We shall assume that spin-lattice relaxation has a negligible effect on the linewidth. Although this assumption should be checked directly in future experiments, it is reasonable on the basis of values of T_{1e} reported on similar samples at higher temperatures.¹⁰ If we omit spin-lattice relaxation as a factor in the linewidth, it follows that ΔH_a is determined by interactions among the spins.

Earlier work on Si:P at low temperatures has shown that the ESR signal seen at this concentration is heavily narrowed, either by exchange or by translational motion.²⁰ In the former case, the line shape is Lorentzian, as observed (Fig. 5). Narrowing by translational motion is usually observed to give a Lorentzian line²¹ as well. Thus, our observed line shape is consistent with the interpretation that the width of the line reflects narrowing of an interaction that would otherwise make it broader.

Before considering what interactions are to be narrowed, we indicate two that do not play a role in the width of the ESR absorption line. The first is the dipolar interaction among the electron spins. At the low concentration in our sample this interaction has been estimated² to be on the order of 10^{-6} K, or 20 kHz, which is negligible. The second is that part of the electronic-spin-exchange interaction that is isotropic in the spin operators, i.e., of the form $\vec{S}_i \cdot \vec{S}_j$, where \vec{S}_i is the spin operator of the i th spin. According to the moment theory of the linewidth,²² this term commutes with the transverse components of \vec{S} , and therefore does not contribute to the second moment of the ESR absorption line. Prior studies of Si:P have indicated that the spin part of the exchange is isotropic. The theoretical work² treats the electronic exchange as purely isotropic in the spin operators. (There is an anisotropy in the spatial part of the exchange interaction² in Si:P, but it does not contribute to the linewidth.²²) Experiments on Si:P with a low donor concentration also show the spin part of the exchange is highly isotropic, as is evident from the fact that a single, narrow line is seen from exchange-coupled pairs in a powdered sample¹¹ of Si:P. This result does not rule out any anisotropy; it only shows that it must be very small. Since these experiments are for very weakly coupled pairs, it may be that in more concentrated samples the exchange interaction becomes sufficiently large that even a small fraction of spin anisotropy becomes important in determining the linewidth. More work is needed to clarify this point.

One of the interactions to be narrowed is the hyperfine interaction of a bound donor electron with the ^{31}P nucleus, which has a spin $I = \frac{1}{2}$ and a natural abundance of 100%. For isolated, bound, donor electrons, this interaction splits the ESR line into two components²³ separated by 42 Oe. In a more concentrated system there are, in principle, three ways that this interaction can be averaged

out to give our observed single line near the midpoint of the hyperfine doublet: (a) the electron moves in an extended band state, so that the overlap of its wave function with the donor nuclei is negligible, and any residual interaction is averaged by the rapid motion of the spin past many donor sites, (b) the electron executes thermally activated hops among donor states rapidly enough that the hyperfine field is averaged to zero, and (c) the electrons are bound to individual donor nuclei, but the exchange interaction among them is strong enough to "exchange-narrow" the hyperfine interaction. Since the first mechanism appears incompatible with the random exchange picture that is so successful at explaining the susceptibility, we drop it from further consideration at and below the concentration covered in our experiments. It is more difficult to distinguish between possibilities (b) and (c), and we shall not attempt to do so here. In fact, it is possible that these two mechanisms could operate together.

If there is some small anisotropy in the spin part of the exchange interaction as mentioned above, it could also have a contribution to the linewidth. In this case, motional averaging could occur for either static or hopping spins. Some broadening of the linewidth is also expected from the hyperfine interaction of the donor electron with the ^{29}Si nuclei. This interaction is responsible for the ESR linewidth and Gaussian ESR absorption line shape of isolated donors.¹⁶ However, since this width is small compared to the hyperfine splitting of the ^{31}P donor nucleus, and it should be narrowed by the same factor, its effect on the linewidth of coupled donor spins is negligible.

Now that we have identified the interactions that could be responsible for $\Delta H_{1/2}$, it would be desirable to analyze quantitatively the observed behavior of $\Delta H_{1/2}$ to show the relative importance of the hyperfine interaction and the spin anisotropy in the exchange interaction, as well as to indicate whether the narrowing is dominated by stationary or hopping spins. Unfortunately, neither the theory nor the experiments are sufficiently well developed yet to accomplish this.

There are, nevertheless, several qualitative points that can be made regarding $\Delta H_{1/2}$. The first is that the narrowing has to involve a large number of exchange-coupled spins or individual spins that hop among many sites. If these conditions are not met, discrete absorption lines should appear,²³ in contradiction to what is observed.

A consequence of this many-body aspect of the narrowing is that the observed width appears to be too large for a narrowed hyperfine line. This follows from the simple statistical result that an electron which rapidly samples the hyperfine interaction with N nuclei will have a hyperfine-related resonance linewidth that is the basic hyperfine splitting reduced by the factor $N^{-1/2}$. The sampling can occur because of rapid hopping among donor sites, or because of rapid spin flips generated by the exchange interaction among the electrons.²⁴ If N is large, as argued above, then the linewidth contributed by the hyperfine interaction must be small compared to the isolated donor splitting. This splitting is ± 21 Oe at high fields in Si:P,²³ but it is only about ± 2 Oe at the highest frequency used in our experiments. This low-field regime is shown in Fig. 9, where the Breit-Rabi diagram²⁵ using the pa-

rameters of Si:P appears.¹⁷ Although we expect that comparison should be made with the smaller value, to our knowledge the theory of this narrowing has not yet been worked out for the random antiferromagnet, and we can not rule out the need to compare $\Delta H_{1/2}$ with the larger figure. The data at 58.2 MHz in Fig. 4 indicate that $\Delta H_{1/2}$ exceeds 10 Oe, and suggests it increases rapidly as T is decreased. Thus, we believe that the linewidth is due, at least in part, to interactions other than the hyperfine interaction with the donor nucleus in Si:P. This conclusion is somewhat tentative, as the divergence at the lowest temperatures is not yet sufficiently well established by the data. It is important for this question to obtain more measurements, and to carry them to lower temperatures and higher fields. From Fig. 7 it is evident that measurements down to 10 mK would bring ΔH_a to the upper limit of the hyperfine interaction corresponding to one electron and one donor nucleus.

Another point to be discussed is the increase in $\Delta H_{1/2}$ which occurs as the temperature is lowered. According to the usual model of an exchange-narrowed line,²⁰

$$\Delta H_{1/2} \approx \omega_a^2 (\gamma_e \omega_e)^{-1}, \quad (2)$$

where ω_a is the frequency of the interaction to be narrowed, γ_e is the electron gyromagnetic ratio, and ω_e is the exchange frequency. In the random exchange system represented by Si:P, it is difficult to assign parameters to ω_a and ω_e . We can, however, point out one feature of random antiferromagnetic exchange models—they should contribute to the temperature dependence of $\Delta H_{1/2}$. It is the tendency of such systems to become "self-diluted" by condensing into singlet ground states of clusters as the temperature is lowered.⁸ One effect of this self-dilution is that the susceptibility rises less rapidly than that of a Curie law. Another effect is that the effective exchange "seen" by the remaining unpaired spins is reduced as the temperature is lowered. If the temperature dependence of $\Delta H_{1/2}$ is dominated by ω_e in Eq. (2), this effect may increase as the temperature is decreased. Although we believe this factor is an important ingredient in the temperature dependence of $\Delta H_{1/2}$, not knowing what to use for ω_a in Eq. (2) makes it impossible to give a more definitive interpretation.

There is an aspect of ESR linewidth that is important for its interpretation that has not been tested in our experiments. It is the question of whether the line is homogeneously or inhomogeneously broadened.²⁶ Both the exchange narrowing and hopping mechanisms of setting the linewidth imply that the line is homogeneously broadened, whereas a random, static distribution of local fields (produced by an as yet unrecognized source) would produce an inhomogeneous contribution. This question is usually answered experimentally by way of "hole burning"²⁷ or spin-echo measurements. The former was not attempted in our work, as the short T_{1e} would have required an amount of power that would have heated the sample too much, and our setup is not able to do the latter.

Our results show that an earlier model proposed by Maekawa and Kinoshita¹² to explain $\Delta H_{1/2}$ at low temperature in the concentration range $(1.1-2.3) \times 10^{18} \text{ cm}^{-3}$ does not apply. That model, which is based on narrowing

by thermally induced hopping among donor states, predicts

$$\Delta H_{1/2} \propto \exp(2R_0/a_0) \tanh(\Delta/2kT), \quad (3)$$

where R_0 , a_0 , Δ , and k are, respectively, the interdonor distance, the effective Bohr radius, the potential difference between an occupied site and an unoccupied one, and Boltzmann's constant. The values $a_0 \approx 25 \text{ \AA}$ and $\Delta \approx 6 \text{ K}$ were assigned¹² to fit their data over the temperature range 1.1–4.2 K. With these values, Eq. (3) predicts that $\Delta H_{1/2}$ should become independent of temperature near 1 K. Since Fig. 7 shows a completely different behavior for $\Delta H_{1/2}$ below 1 K, we conclude that this hopping model does not explain the ESR linewidth.

From a purely phenomenological point of view, the power-law divergence shown in Fig. 7 suggests a critical behavior headed towards a phase transition at $T=0$, in much the same way as the susceptibility (Fig. 6) and the internal field (discussed below).

C. Internal field

First, we consider the appearance of the internal field at low temperatures. As mentioned earlier, the slope of the points on Fig. 2 show that in this range of magnetic field, the shift in the resonance field corresponds to an H_i that is independent of H_0 . It is not a g shift. There is some hint of a deviation at the highest value of ω , but confirmation of a different behavior at high ω will require extending these measurements to much higher frequencies. The temperature dependence of H_i , taken from Fig. 3, is replotted in Fig. 8 (the solid line through the 11.5-MHz points is a guide to the eye). Although there is a substantial scatter in the data, we believe the trend indicated by the straight line is a fair characterization of the data. In spite of a larger uncertainty in the 58.2-MHz data (the line is broader), a similar behavior is indicated, but with H_i about 40% smaller.

To our knowledge, there is not yet a theory for this kind of local field in an amorphous antiferromagnet such as Si:P. Therefore, as in the case of the linewidth, our dis-

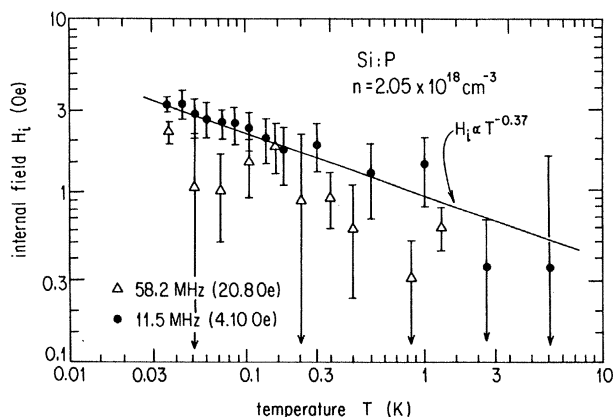


FIG. 8. Internal fields as a function of temperature for Si:P doped to $n = 2.05 \times 10^{18} \text{ cm}^{-3}$ at two values of the applied field. The solid line is a guide to the eye.

ussion will be qualitative and speculative. We begin by ruling out several interactions as responsible for H_i on the basis of their magnitude relative to kT , starting with the donor hyperfine interaction. This can be done by starting with an isolated donor in a magnetic field of about 20 Oe (3 mK) at our lowest temperature of 35 mK. From Fig. 9 it is seen that there would be two hyperfine lines with a splitting of about $\pm 2 \text{ Oe}$, which we think of as being averaged when motional or exchange averaging occurs on the part of the donor electron. A temperature-dependent shift to the resonance then occurs as the lower levels are preferentially populated with decreasing T . The maximum shift, which corresponds to nearly complete population of level a , would be about 2 Oe (we neglect the overall loss of intensity due to the population of level d). Roughly speaking, this figure should be reduced by the factor $\hbar\omega_e/2kT \approx 0.05$ to give 0.1 Oe at 35 mK. This result is an order of magnitude smaller than the observed value, and predicts $H_i \propto 1/T$, in contradiction to what is observed. In addition, it predicts a shift that is 25 times smaller at 11.5 MHz, and a decrease in the field for resonance in an experiment done at constant frequency. These points also conflict with our observations. Thus, we conclude that the origin of H_i is not the hyperfine interaction with the donor nuclei. Similar arguments apply for the even smaller hyperfine interaction with the nearby ^{29}Si nuclei ($\approx 0.3 \mu\text{K}$) and the dipolar interaction between donors ($\approx 1 \mu\text{K}$).

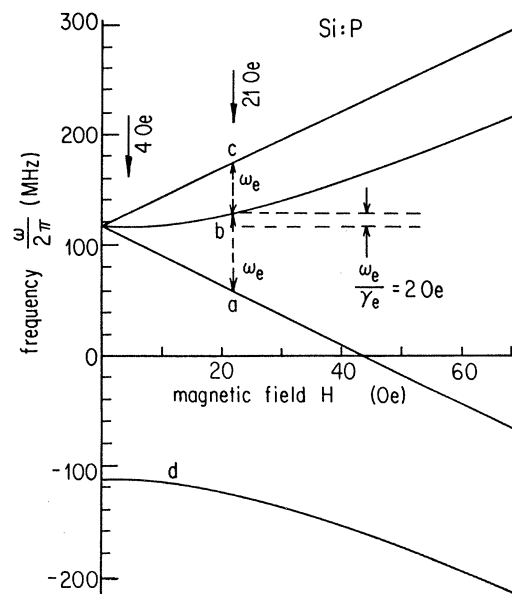


FIG. 9. Energy-level diagram of an electron bound to an isolated ^{31}P donor in Si as a function of magnetic field in the low-field regime. Following Ref. 17, the zero-field hyperfine splitting is 42 Oe and the g value is 2.00. The two solid arrows indicate the magnetic fields used to most of our measurements. The dashed lines show that the two ESR lines for an isolated donor at 21 Oe have a hyperfine splitting of 2 Oe. Although this is one of the interactions to be narrowed, it is too small to account for the ESR linewidth reported in Fig. 4.

The main interaction left is the exchange interaction among the donors. The divergent, non-Curie behavior of χ has already been explained in terms of it in Si:P.^{2,18,8,9} We suggest that the appearance of H_i is due to the same interaction. This situation is similar to the case of a spin-glass²⁸ above the spin-glass transition temperature (T_g),

where both the non-Curie χ and the internal field are attributed to the exchange interaction between the spins. It differs from the REHAC, where it has been proposed that the internal field is associated with the crossover to a 3D dipolar interaction among the electrons.²⁹ Since, however, there is not yet a theory of internal field in Si:P, we can-

TABLE I. Comparison of representative experimental properties and interactions of the amorphous antiferromagnet, spin-glass, and REHAC. (?) indicates that the point has been proposed, but is not yet well established.

Property or interaction	Amorphous antiferromagnet Si:P ($n \approx 2 \times 10^{18} \text{ cm}^{-3}$)	Spin-glass Ag:Mn ($n \approx 2.5 \text{ at. \%}$)	REHAC [Qn(TCNQ) ₂]
Important magnetic interactions	3D random antiferromagnetic exchange + Zeeman + electron dipole-dipole (?) + hyperfine ^{a-c}	3D random RKKY + anisotropic exchange + electronic dipolar ^d	1D random antiferromagnet + electron dipolar (?) + electron-nuclear dipole and exchange ^{e,f}
Behavior of low-field low-temperature magnetization	Nearly $T^{-\alpha}$ with α approximately 0.66 down to 30 mK, nearly independent of T below 30 mK ^{a,b}	Cusp at T_g ^g	$T^{-\alpha}$ down to 8 mK, crossover to dipolar behavior (?) at lower T ^{e,h}
Interaction responsible for low-temperature magnetization	3D random antiferromagnetic exchange down to 30 mK, (?) below 30 mK ^{a,b}	3D random RKKY interaction ^g	1D random exchange, crossover to 3D dipolar (?) below 8 mK ^{e,h}
Behavior of ESR linewidth with decreasing temperature	Increases with power-law divergence towards $T=0$ (?) ^a	Increases with power law divergence towards $T=T_g$ ^d	Increases logarithmically with divergence at $T=0$ in REHAC region, complex behavior in crossover region ^{f,h}
Behavior of ESR linewidth with increasing external magnetic field	Increases at low field (4–20 Oe) ^a	Decreases just above T_g ^d	Decreases logarithmically at low field in REHAC region ^f
Mechanism for linewidth at low T	Narrowing of anisotropic exchange (?) and hyperfine interactions by hopping (?) and exchange ^a	Exchange narrowing of anisotropic exchange and electron-dipolar interactions (?) ^d	Exchange narrowing of electron-nuclear, electron-dipolar, and anisotropic exchange (?) interactions ^f
Direction of internal "field"	Opposite external field ^a	Along external field ^d	Along external field ^h
Behavior of internal "field" with decreasing temperature	Power-law divergence to $T=0$ ^a	Power-law divergence to $T=T_g$ ^d	Diverges as T^{-2} at high temperature, saturates (?) at lower T ^h
Mechanism for internal "field"	Not established ^a	Exchange field ^d	Not established ^h

^aThis work.

^bReference 2.

^cReference 8.

^dReference 28.

^eReference 6.

^fReference 32.

^gReference 9.

^hReference 29.

not propose a definite explanation of its origin.

The orientation of the internal field *opposite* to the applied field is also unexplained. It may reflect the fact that the sign of the microscopic interaction among the donor spins is primarily antiferromagnetic.³⁰ This orientation of H_i is opposite to that reported for the REHAC, quinolinium di-tetracyanoquinodimethanide [Qn(TCNQ)₂], where an internal field oriented *along* the external field emerges at low temperatures.²⁹ Since the REHAC has an effective spin-spin interaction which crosses over mainly to dipolar at the lowest temperatures, i.e., has a mixture of both "antiferromagnetic" and "ferromagnetic" signs, it may be that this distribution of sign in the random interaction is the primary factor which determines the direction of the internal field relative to the applied field. An analogous alternation in the sign of the interaction occurs for the Ruderman-Kittel-Kasuya-Yosida (RKKY) spin-glass Ag:Mn,²⁸ where the divergent internal field caused by the interactions (and the external magnetic field) is oriented along the external field. In this case, the divergence is toward the spin-glass transition temperature instead of 0 K.

Evidence for an "internal field" has also been seen from the behavior of the shift in the position of the spin-flip Raman scattering in the amorphous antiferromagnet *n*-type CdS when a large magnetic field is applied.²³ These experiments were interpreted in terms of a field-induced exchange stiffness, which was related to the random antiferromagnetic exchange. The observed effects had the character of an internal field pointing opposite to the external field, as it does in Si:P. Because the observations in *n*-type CdS were made at such high fields, it is difficult to tell if the phenomenon is related to H_i seen in our measurements.

D. Electron-spin relaxation time

We interpret the short value we observed for T_{1e} (≤ 1 ms) down to the lowest temperatures as due to relaxation between the electron Zeeman and exchange reservoirs, and not related to the long relaxation times expected of isolated donors in Si:P at low temperatures.²⁷ This explanation of such behavior by exchange-coupled electron-spin systems has been known for a long time.³¹ It has already been used to explain T_{1e} in Si:P at higher temperatures,²⁷ and can lead to rapid spin relaxation down to very low temperatures.³²

E. Comparison with other random spin systems

The phenomena presented here for submetallic Si:P have features that in some cases resemble, and in others, differ from, two other random exchange systems: the RKKY spin-glass above T_g and the REHAC. Because of their similarities and differences, it is useful to put the magnetic properties of Si:P into perspective relative to the

other two. This is done in Table I, where the representative cases of Ag:Mn for a spin-glass and Qn(TCNQ)₂ for a REHAC are compared with Si:P.

There are two comments to be made regarding Table I. The first is the nature of the internal field. On the basis of experiments in spin-glasses over a wide range of applied fields,^{28,33} there is controversy about whether the shift in position of the ESR should be described as an internal field, a *g* shift, or something intermediate between the two. The first implies a resonance shift independent of the applied field, whereas the second implies one that is directly proportional to it, as if the shift could be expressed in terms of a field-independent susceptibility. At present, it is not clear whether these differences reflect fundamentally different kinds of spin-glass behavior, or simply that the various materials explore different regions of the same parameter space. In Table I this uncertainty is recognized implicitly by reference of the internal "field." The other point is that experimental behavior that is not yet well established or interpretations that are still speculative are indicated by (?) in the entry.

V. CONCLUSIONS

We have reported low-field ESR measurements in submetallic Si:P ($n = 2.05 \times 10^{18} \text{ cm}^{-3}$) over the temperature range 0.035–4.2 K. These measurements demonstrate the existence of an internal field and an increased ESR linewidth, both of which diverge as the temperature is lowered. The internal field is aligned opposite to the applied field, and does not exhibit any observable hysteresis. Although there is no quantitative theory with which to compare these experimental results, consideration of several interactions indicates that some can be discarded, and that the major role is played by random antiferromagnetic interactions. The measurements also confirm the non-Curie behavior reported in static measurements and interpreted in terms of the amorphous antiferromagnetic model.^{2,8,9,13} An upper limit of 1 ms is obtained for the electron-spin–lattice relaxation time over the entire temperature range, and it is attributed to the usual relaxation of the Zeeman to the exchange reservoir in exchange-coupled systems.³¹

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