Spin Localization in Si:P—Direct Evidence from ^{31}P Nuclear Magnetic Resonance

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The normalized intensities of the ^{31}P NMR spectra in Si:P decrease when the phosphorus content is lowered through the concentration n_c for the metal-insulator transition. The ^{31}P NMR shift is maximum for $n \simeq 1.1 n_c$ and becomes very small for $n \simeq n_c$. For $n \simeq 1.2 n_c$ the electronic susceptibility χ on the observed nuclei does not follow the T variation of the macroscopic susceptibility but has all the characteristics expected for a Pauli electron gas. Already above n_c, disorder and correlations therefore induce spin localization on an inhomogeneous scale in uncompensated semiconductors.

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Since the recent progress[1] in the theory of metal-insulator transitions (MIT), a large effort has been devoted to the study of various disordered systems displaying such transitions. The disagreement between the exponent 1, expected theoretically for the conductivity σ vs $n - n_c$ for transitions purely driven by disorder, and the exponent $\frac{1}{2}$, found experimentally in uncompensated Si:P,[2] has established that electron-electron interactions are indeed a major ingredient at the transition in these systems. These results have triggered intensive efforts to characterize better the magnetic properties at the transition. A large enhancement of χ_e at low T on the metallic side[3,4] of the MIT has been evidenced by ESR measurements. It is essential to understand whether this enhancement is linked with a large density of excitations in a highly correlated electron gas[5] or with a spin localization.[6] Very decisive information is expected from experiments allowing one to probe locally the electron gas, such as NMR. A large enhancement of the ^{29}Si nuclear relaxation rate[7,8] at low T has been evidenced, but might be explained by either picture, inasmuch as the information on local susceptibilities is not available. A distinct model has been recently proposed on the basis of old pioneering double-resonance experiments.[9] While previous ^{31}P NMR data[10] were limited to $n \gtrsim 2n_c$, in this Letter we present new results taken through the MIT with an optimized sensitivity, which definitely establish the existence of spin localization in Si:P. Indeed, the observed ^{31}P NMR signal has a Knight shift and a relaxation rate T_1^{-1} quite characteristic of a Pauli electron gas, but is only associated with a *fraction of the nuclei which steadily decreases through the MIT.* It is demonstrated that the T-dependent part of χ_e is associated with the nuclei wiped out of the ^{31}P detected NMR. These results therefore imply an inhomogeneous description of the magnetization already on the metallic side of the transition. Further, in contradistinction to macroscopic observations, a dramatic change of the local magnetic properties is shown to occur at the transition.

The data have been taken on commercial single-crystal samples which have been cut into thin slices (200–300-μm thick). The concentration was obtained from the room-temperature resistivity with use of the Mousty scale or from the resistivity ratio[2] $R_{300\,\mathrm{K}}/R_{4.2\,\mathrm{K}}$ for samples near $n_c = 3.74 \times 10^{18}$ cm^3. The NMR samples have been obtained as an assembly of about ten plates exhibiting identical room-temperature resistivities (or RR for $n \simeq n_c$). Most of the results presented here have been taken with standard pulsed NMR techniques, for $H_0 = 20$ kG in experimental conditions leading to the optimal signal-to-noise ratio.

The NMR spectra (Fig. 1) agree with those reported for $n > 2n_c$.[10] The average ^{31}P Knight shift $\langle K \rangle$ measured at 4.2 K on the observed signal increases with decreasing n, but we find that *$\langle K \rangle$ reaches a maximum for $n \simeq 1.1 n_c$ and decreases abruptly for $n \lesssim n_c$. Further, the relative NMR signal intensity[11] x is seen to decrease steadily with decreasing n.* These results are displayed quantitatively in Fig. 2.

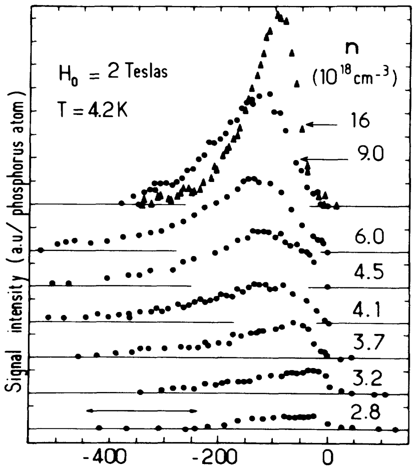

FIG. 1. NMR spectra obtained as time integrals of the spin echo, plotted vs the applied field H. H_0 is the resonance field for a H_3PO_4 salt. The position of the ^{31}P signal of Ref. 9 for $n = 2.5 \times 10^{18}$ cm^3 is given by an arrow.

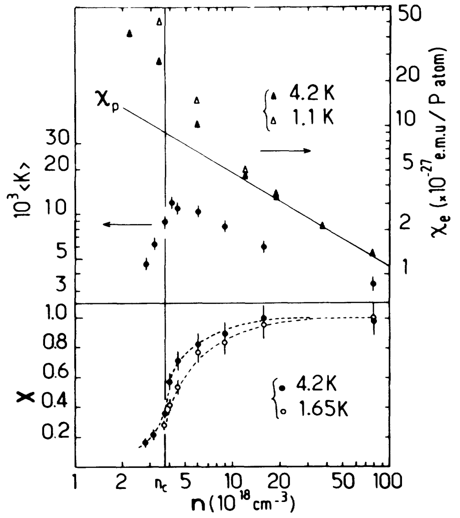

FIG. 2. The average NMR shift $\langle K\rangle$ taken on the (-500 G, 0) field range, and the relative number of detected nuclei x, derived (Ref. 11) from the data of Fig. 1, plotted vs n. The data for χ_e (Ref. 12) and the calculated χ_p are shown for comparison. The dotted lines are guides to the eye.

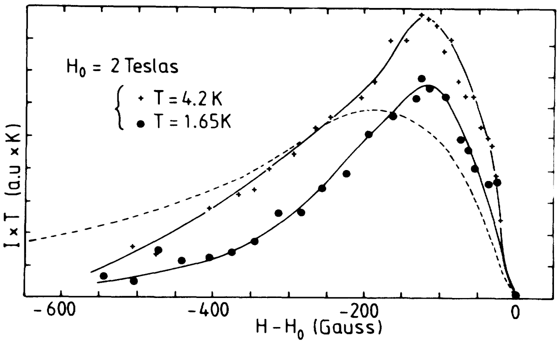

FIG. 3. NMR spectra taken at 4.2 and 1.65 K for $n = 4.5\times 10^{18}/\mathrm{cm}^3$. The data have been normalized for the Curie dependence of the nuclear magnetization and for the spin-echo decay (Ref. 11). The full lines are guides to the eye. The dotted line is the expected spectrum at 1.65 K, without intensity loss, and with the assumption that K_i scales with χ_e.

In a disordered metallic system, the NMR shift for a nucleus at site i is given by

$$K_i = H_i^{\mathrm{hf}}\chi_i/g\mu_{\mathrm{B}}, \tag{1}$$

where the possibility for distributed values of the hyperfine field H_i^{hf} and of the local susceptibility per electron $\chi_i = g\mu_{\mathrm{B}}\langle S_{Zi}\rangle/H_0$ has been included. For $n \gg n_c$, χ_e (the susceptibility given by ESR data) was found T independent[12] and agrees with χ_{P}, the Pauli susceptibility for free electrons in the conduction band of Si. This allowed us to assume that $\chi_i \equiv \chi_{\mathrm{P}}$, in which case the width of the observed ^{31}P NMR was then attributed to a distribution of H_i^{hf}, that is, of the electronic wave function on the nuclear site $\langle |\psi_i(0)|^2\rangle$, averaged at the Fermi level.[10] However, no experimental technique could allow us to separate out an eventual distribution of χ_i. Below $n \simeq 2n_c$, χ_e increases much faster than χ_{P}, while $\langle K\rangle$ goes through a maximum (Fig. 2). *The electronic susceptibility sensed by the observed ^{31}P is then much smaller than χ_e.* It can also be seen that the NMR intensity loss is directly correlated with the deviation of χ_e with respect to χ_{P}. Therefore, below $n \simeq 2n_c$ a large part of χ_e is associated with those ^{31}P nuclei which are wiped out of the observed spectrum. This is further emphasized by a direct comparison of the NMR spectra taken at 4.2 and 1.65 K (for $n \simeq 1.2n_c$, Fig. 3). While a 50% increase of χ_e (Ref. 12) occurs in this T range, the ^{31}P NMR only displays minor changes. Although an intensity loss is detected, the distribution of Knight shifts is nearly insensitive to the change of χ_e. We could measure the nuclear spin-lattice relaxation time T_1 at various field positions on the NMR spectrum, for $K < 10^{-2}$ for which the signal-to-noise ratio was sufficient. The data follow a Korringa relation,

$$T_{1i}TK_i^2 = s\gamma_e^2/4\pi k_{\mathrm{B}}\gamma_n^2, \tag{2}$$

within experimental accuracy in the ^{4}He temperature range (Fig. 4). This allows us to conclude that our observation restricts us to those ^{31}P nuclei which are somewhat distant from the regions of spin localization, and are rather coupled to a Pauli-type electron gas, for $n_c < n < 2n_c$.

To estimate the Pauli susceptibility of the associated electron states, we might assume that the hyperfine field is nearly unchanged with respect to the value for isolated donors ($H_{at}^{\mathrm{hf}} \simeq 68$ kG).[13] Indeed, near n_c the overlap between orbitals becomes small enough as the distance between donors is about four times the Bohr radius. The

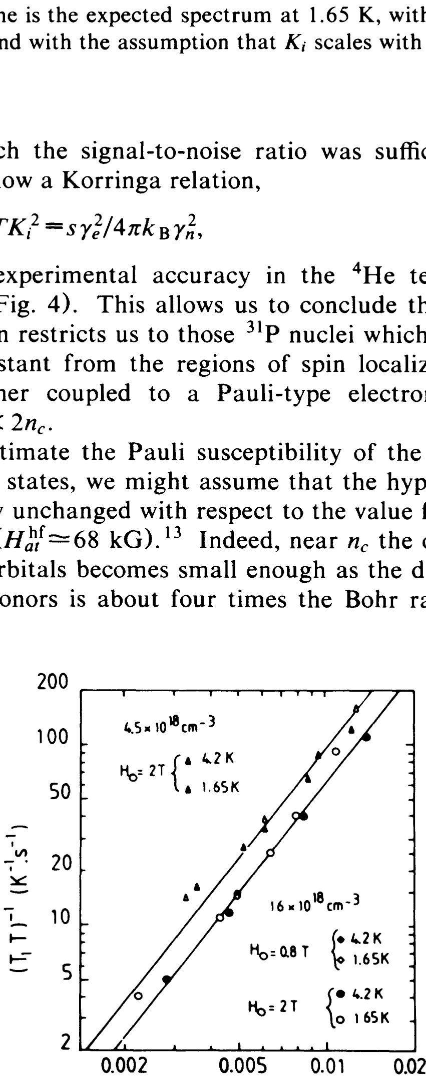

FIG. 4. $(T_{1i}T)^{-1}$ data taken along the NMR spectra. The full lines represent Eq. (2) with $s = 0.6$ and 1.06, respectively, for $n = 1.2n_c$ and $5n_c$.

susceptibility associated with the peak Knight shift of the NMR signal of Fig. 3 corresponds then to $\chi_0 \simeq 0.22\chi_P$. This might be tentatively assigned to a low electronic density of states in a broad impurity band[14] and/or to a contribution at the Fermi level of P^- states in the upper Hubbard band.[1] In any case, such a low value for χ_0, and the measured Korringa constant ($s=0.6$), altogether exclude any ferromagnetic extended correlations in the corresponding electron gas near the transition.[9] This small reduction of s might rather originate from slight antiferromagnetic correlations or eventually from a small contribution to T_1^{-1} of the distant electrons responsible for the paramagnetic terms in χ_e.

For $n \lesssim n_c$ the susceptibility associated with the observed states is more than one order of magnitude smaller than χ_P and would then correspond either to electrons bound to antiferromagnetically coupled donors or to P^- states. Unfortunately the experimental sensitivity was so low that reliable studies of the T dependence of the spectrum or of T_1 could not be performed. However, our data have nothing in common with those obtained 25 years ago by Jérome *et al.*[9] by a double-resonance technique. These authors detected a broad shifted ^{31}P NMR signal on a $2.5\times10^{18}/\text{cm}^3$ sample with a long enough T_1 to be easily detectable in our experiment, if associated with a majority of the ^{31}P spins. It can rather be emphasized from our results that their signal is due to much less than 10% of the ^{31}P nuclei.

As for the nuclei which are wiped out of the NMR signal, with the assumption that they sense the average excess susceptibility $\chi_l=(\chi_e - x\chi_0)/(1-x)$, their resonance (for $T=4.2$ K and $n=1.2n_c$) should be shifted by about 2000 G, far below our experimental sensitivity. It seems to us quite natural to consider that these states, which bear all the T dependence of χ_e, are localized on groups of P atoms, as $\chi_l \simeq 0.35\chi_C$, where $\chi_C=\mu_B^2/kT$ is the Curie susceptibility for a free spin. We show hereafter that these states are responsible for the large enhancement of $(T_1T)^{-1}$ of ^{29}Si detected at low T.[7,8] Indeed, for a nuclear spin at site i coupled through a scalar interaction with the electronic magnetization, either localized or extended,

$$(T_{1i})^{-1}=k_BT(\gamma_n H_i^{\text{hf}}/g\mu_B)^2\chi_i\tau_i/(1+\omega^2\tau_i^2), \qquad (3)$$

with the simple assumption that the local magnetization has an exponential correlation function (with τ_i as a correlation time). The enhancement of $(T_{1i}T)^{-1}$ therefore certainly signals that χ or τ (or both) is enhanced at low T. However, these quantities can only be derived from simultaneous measurements of K_i and T_{1i}. This has not been done in most previous experiments as, for $n \simeq n_c$, H_i^{hf} and K_i are quite small on the vast majority of Si sites.[7,8] Even nuclei involved in the surroundings of "magnetic" states do then contribute to the ^{29}Si NMR, while the corresponding ^{31}P nuclei are wiped out in our observations.

Hirsch and Holcomb[15] have been able recently to measure T_{1i} vs K_i for ^{29}Si in high fields ($H_0 \simeq 6$ T) at 4.2 K, for $n \simeq 1.3n_c$. They detect a nonexponential recovery of the nuclear magnetization and estimate a "Korringa"[16] constant $s \simeq 0.25$ quite smaller than $s \simeq 0.6$ obtained here for ^{31}P ($s \simeq 1$ is obtained for both nuclei for $n \gg n_c$).[7] These are clear indications that even at 4.2 K the ^{29}Si are more influenced by the localized part of the magnetization. A further consequence of the weakness of the induced local fields on ^{29}Si is that diffusion of nuclear-spin magnetization certainly occurs between ^{29}Si, while it is completely prohibited between ^{31}P nuclei (Fig. 4). In the former case, although a direct mapping of the situation encountered in dilute alloys onto the present problem is not straightforward, one does expect that spin diffusion will be increasingly inhibited near magnetic centers when their magnetization increases,[17] which might explain at least partly the H_0 variation of $^{29}T_1$. We can therefore conclude from this comparison of ^{29}Si and ^{31}P NMR data that the inhomogeneous description of the electron gas, as well as the incidence of nuclear-spin diffusion, must be taken into account to be able to discuss in detail the significance of the $^{29}T_1$ data.[18]

While it has been sometimes considered that the existence of a single narrow ESR line implied a homogeneous behavior of the electron gas, our results rather establish that a localized part of the magnetization appears above n_c and progressively takes more importance with decreasing n. The narrow ESR for $n > n_c$ results from strong spin exchange between the localized and extended magnetization, a situation which is well known to prevail in dilute alloys[17] (the so-called bottleneck effect for *Cu*Mn ESR). One can easily understand then that measurements of χ_e and $^{29}T_1$, which are more sensitive to the localized part of the magnetization, do not show any strong anomaly at n_c. Although an empirical subdivision of the measured χ_e into Pauli and Curie parts was proposed some time ago,[12] the present work is the first unambiguous experiment allowing some microscopic insight into this inhomogeneous description. The Pauli electron states are found here to correspond to a low susceptibility, as for a broad impurity band, and/or a contribution of P^- states at the Fermi level. This excludes a narrow band with an enhanced susceptibility,[9] a highly correlated electron gas,[5] as well as a simple χ_p contribution of n electrons in the Si conduction band. Recent renormalization-group procedures[6] applied to models involving both disorder and correlations suggest an increase of χ_e together with a decrease of the spin diffusion constant for decreasing T, which is in qualitative agreement with the present observations, as well as with the low-T broadening of the ESR line.[4] Alternatively, the approach of Bhatt and Lee,[19] developed for $n < n_c$ to explain the T dependence of χ_e below 1 K, might as well be extended to describe the localized susceptibility near n_c

on the metallic side of the transition. As our experiments indicate that $1-x$, which represents approximately the fraction of localized states, increases at low T, further experimental as well as theoretical estimates of $x(T, n-n_c)$ might help to distinguish among these approaches. It would indeed be of great interest to determine whether a Pauli contribution to χ_e is retained down to $T=0$. This would require an extension of our measurements to lower temperatures for $n > n_c$, which is unfortunately not easy to undertake. Further sensitivity improvements, for instance with the help of double resonance techniques, would help to get a deeper insight on the local properties especially below n_c, as T_1 measurements could not be performed in this T range.

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