NMR investigation of the diluted magnetic semiconductor 
Li(Zn_{1-x}Mn_{x})P (x=0.1)
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The successful fabrication of (Ga$_{1-x}$Mn$_x$)As ferromagnetic thin films by molecular beam epitaxy (MBE) techniques\(^2\) generated great interest in the research into diluted magnetic semiconductors (DMS)\(^2\). The quality of the epitaxial films steadily improved, and the Curie temperature, \(T_c\), has reached as high as 190 K at the doping level of \(x = 12\%\).\(^3\) The spintronic applications of the DMS may soon become a reality once the \(T_c\) exceeds room temperature\(^4\). Nonetheless, understanding the physical properties of the DMS remains a major challenge\(^5\). A fundamental difficulty stems from the fact that the synthesis of the bulk form of (Ga$_{1-x}$Mn$_x$)As is impossible beyond the very low solubility limit of \(x \sim 1\%\), excluding the possibilities to employ typical microscopic probes of magnetism, such as NMR and neutron scattering techniques.

Recently, Deng et al. reported the successful synthesis of a bulk Li(Zn$_{1-x}$Mn$_x$)As DMS with \(T_c\) as high as \( \sim 50\) K based on the I-II-V direct-gap semiconductor LiZnAs\(^9\). The structure of LiZnAs, shown in Fig. 1(a), can be viewed as an analogue of GaAs with the Zinc-blend structure, see Fig. 1(b); notice that if we replace Ga$^{3+}$ sites of GaAs with Zn$^{2+}$ and place Li$^+$ ions between Zn$^{2+}$, we obtain LiZnAs. Also notice that the total number of electrons in (ZnAs)$^-$ is equal to that of GaAs. LiZnAs has a direct band gap of \(\sim 1.6\) eV\(^12\)-\(^15\), which is comparable to that of GaAs (1.42 eV). On the other hand, the isovalent substitution of Mn$^{2+}$ for Zn$^{2+}$ resembles that of II-VI DMS, although it is difficult to control the carrier density in the latter\(^10,11\). Recent µSR measurements of Li(Zn$_{1-x}$Mn$_x$)As\(^9\) have established that the magnetically ordered volume reaches 100 \% below \(T_c\), and the magnitudes of the ferromagnetic exchange coupling and the ordered moment are comparable to those of (Ga,Mn)As\(^16\). More recently, some of us\(^17\) found that the iso-structural direct-gap semiconductor LiZnP\(^12,18\) also undergoes a ferromagnetic transition upon Mn doping, and its bulk magnetic properties are very similar to those of LiZnAs.

In this paper, we use $^7$Li NMR to investigate LiZn$_{0.9}$Mn$_{0.1}$P (\(T_c = 25\) K). Since NMR probes the electronic properties in the immediate vicinity of the observed nuclear spins, our NMR measurements will provide local and site-selective information for LiZn$_{0.9}$Mn$_{0.1}$P. In this context, it is worth recalling that NMR measurements provided vital microscopic information on the nature of dilute magnetic spins doped into, e.g. simple metals\(^19\) and high \(T_c\) superconductors\(^20\). By successfully identifying $^7$Li NMR signals arising from the nearest-neighbor (n. n.) Li site of doped Mn (denoted as high as \(\sim 50\) K based on the I-II-V direct-gap semiconductor LiZnAs\(^9\). The structure of LiZnAs, shown in Fig. 1(a), can be viewed as an analogue of GaAs with the Zinc-blend structure, see Fig. 1(b); notice that if we replace Ga$^{3+}$ sites of GaAs with Zn$^{2+}$ and place Li$^+$ ions between Zn$^{2+}$, we obtain LiZnAs. Also notice that the total number of electrons in (ZnAs)$^-$ is equal to that of GaAs. LiZnAs has a direct band gap of \(\sim 1.6\) eV\(^12\)-\(^15\), which is comparable to that of GaAs (1.42 eV). On the other hand, the isovalent substitution of Mn$^{2+}$ for Zn$^{2+}$ resembles that of II-VI DMS, although it is difficult to control the carrier density in the latter\(^10,11\). Recent µSR measurements of Li(Zn$_{1-x}$Mn$_x$)As\(^9\) have established that the magnetically ordered volume reaches 100 \% below \(T_c\), and the magnitudes of the ferromagnetic exchange coupling and the ordered moment are comparable to those of (Ga,Mn)As\(^16\). More recently, some of us\(^17\) found that the iso-structural direct-gap semiconductor LiZnP\(^12,18\) also undergoes a ferromagnetic transition upon Mn doping, and its bulk magnetic properties are very similar to those of LiZnAs.

In this paper, we use $^7$Li NMR to investigate LiZn$_{0.9}$Mn$_{0.1}$P (\(T_c = 25\) K). Since NMR probes the electronic properties in the immediate vicinity of the observed nuclear spins, our NMR measurements

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig1.png}
\caption{(Color online) The crystal structure of (a) LiZnP, and (b) GaAs. The representative $^7$Li lineshapes in 4 Tesla of (c) the parent compound LiZnP, and (d) LiZn$_{0.9}$Mn$_{0.1}$P. The vertical arrow marks Li(Mn), the n. n. site of doped Mn.}
\end{figure}
as the Li(Mn) site hereafter), we were able to probe the static and dynamic properties of Mn magnetic moments using NMR in the paramagnetic state of DMS for the first time.

The polycrystalline LiZnP and LiZn0.9Mn0.1P were synthesized by the solid state reaction method. High purity elements of Li (99.9%), Zn (99.9%), Mn (99.99%), and P (99%) were mixed and slowly heated to 450°C in evacuated silica tubes, and held for 48 hours before cooling down to room temperature at the rate of 20°C/h. X-ray diffraction showed that both specimens are single phase with a cubic structure. The lattice constants are 5.7371 Å and 5.7434 Å for LiZnP and LiZn0.9Mn0.1P, respectively. We also confirmed from the dc-magnetization and µSR measurements that the ferromagnetic ordering is of bulk nature with \( T_C = 25 \) K. The Hall effect measurements conducted for samples prepared under the identical conditions showed that LiZn0.9Mn0.1P is a hole-doped semiconductor with a very low carrier concentration of \( p \sim 3 \times 10^{17} \text{ cm}^{-3} \). We will report the complete details of synthesis and characterization of the LiZn0.9Mn0.1P sample by X-ray diffraction, electrical resistance, and µSR elsewhere.17

We show representative \(^7\)Li NMR lineshapes of the parent compound LiZnP in Fig. 1 (c). \(^7\)Li has nuclear spin \( I = \frac{3}{2} \), and the gyromagnetic ratio is \( \frac{\gamma_n}{2\pi} = 16.546 \text{ MHz/Tesla} \). In the external magnetic field \( B_{ext} = 4 \) Tesla, resonance would take place at \( f_0 = \left( \frac{\gamma_n}{2\pi} \right) B_{ext} = 66.184 \text{ MHz} \) in the absence of hyperfine interactions with electrons. In general, three NMR peaks for the \( I_z = m \) to \( m+1 \) transition (\( m = -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2} \)) could arise for each inequivalent Li site, if there exists significant interaction between the nuclear quadrupole moment and the electric field gradient (EFG). For the parent compound LiZnP only one Li peak is observed at \( f_0 \sim 66.206 \text{ MHz} \), as shown in Fig. 1(c). This is because Li atoms are located in a nearly cubic environment, and the EFG is extremely small due to the high symmetry of the lattice. The half height full width (HHFW) of this peak is \( \sim 5 \text{ KHz} \) at 290 K, indicating the high quality of the polycrystalline sample. The very small NMR Knight shift (a.k.a. the paramagnetic frequency shift)\(^{21} \), \( \frac{\gamma_n}{2\pi} = (66.206-66.184)/66.184 = 0.003 \) (i.e. \( +0.03 \% \), or \( +300 \text{ ppm} \)), is consistent with the absence of conduction electrons or magnetic moments.

The substitution of Mn drastically alters the \(^7\)Li NMR lineshape of LiZn0.9Mn0.1P as shown in Fig. 1(d). To enhance the extra features, we plot the temperature dependence of \(^7\)Li NMR lineshapes in a semi-logarithmic scale in Fig. 2. In addition to the relatively sharp but somewhat asymmetrical Li(0) peak that corresponds to the single peak of LiZnP, a broad hump appears on the lower frequency side, as marked by a downward arrow in Fig. 1(d) and the shadowed area in Fig. 2. This broad hump should be attributed to Li(Mn) sites whose magnetic environment is altered by the substitution of the Zn\(^{2+}\) sites in their vicinity by Mn\(^{2+}\) ions. Upon decreasing the temperature from 280 K to 30 K, the Li(Mn) peak shifts progressively towards lower frequencies, and becomes as broad as 3 MHz. These striking features of the Li(Mn) peak should be attributed to the spin polarization transferred from the n. n. Mn sites through weak but finite hybridizations between Mn 3d and Li orbitals. We define the NMR Knight shift of the Li(Mn) sites at the center of the broad hump, as marked by downward arrows in Fig. 2. We summarize the temperature dependence of \( -\frac{\gamma_n}{2\pi} \) measured in \( B_{ext} = 4 \) T for the Li(Mn) sites in Fig. 3. \(-\frac{\gamma_n}{2\pi}\) exhibits identical temperature dependence to the bulk magnetization \( M \) as measured by...
SQUID in \( B_{\text{ext}} = 4 \) T (solid curve). Also presented in the inset is \( M \) measured in \( B_{\text{ext}} = 0.01 \) T, establishing the bulk ferromagnetism below \( T_c = 25 \) K. In general, \( ^7K = ^7K_{\text{spin}} + ^7K_{\text{orb}} = (A_0/g\mu_B)\chi_{\text{spin}} + ^7K_{\text{orb}}. \)

The small orbital shift \( ^7K_{\text{orb}} \) is temperature independent \((\sim +0.05\% \text{ in the present case})\), while the hyperfine coupling between the Mn electron spins and the Li nuclear spin, \( A_0 = -12 \) kOe/\( \mu_B \), turns out to be negative for the Li(Mn) peak, hence the overall sign of \( ^7K < 0 \). Note that \(-^7K\) reaches as large as 3.5%.

In contrast with the Li(Mn) sites, \( ^7K \) at Li(0) remains small and comparable to that in nonmagnetic LiZnP (see Fig. 1). The HHFW of Li(0), however, is much broader than that of LiZnP \((\sim 5\) KHz\), and continuously increases from 20 KHz at 280 K to 240 KHz at 4.2 K. The fact that HHFW of Li(0) is an order of magnitude broader in LiZn0.9Mn0.1P suggests that the hyperfine magnetic fields from the doped Mn strongly affect all Li sites, including those without Mn atoms at n.n. Zn sites. Our findings in Fig. 3 are consistent with our \( \mu \)SR results observed for the same sample that the ferromagnetic volume fraction reaches 100% \(^1\).\(^1\)

To gain additional insight into the nature of Mn spins, we also measured the nuclear spin-lattice relaxation rate \( T_1^{-1} \) at the Li(0) peak and the center of the broad Li(Mn) peak, as marked by downward arrows in Fig. 2. We note that we do not observe satellite peaks corresponding to the \( \pm \frac{1}{2} - \pm \frac{3}{2} \) transitions for both Li(0) and Li(Mn) sites. This is not surprising, in view of the fact that even the Li(Mn) sites are still located in a high symmetry environment: Mn\(^{2+} \) ions are isovalent with Zn\(^{2+} \) ions, and the difference between the ionic radius of Mn\(^{2+} \) \((0.083 \text{ nm})\) and that of Zn\(^{2+} \) \((0.074 \text{ nm})\) is small. We also confirmed that the radio frequency pulse width optimized for the Li(Mn) and Li(0) peaks is identical with that of LiZnP, implying that the Li(0) peak does not arise from the \( +\frac{1}{2} \) to \(-\frac{1}{2} \) transition alone. If the sharper Li(0) peak in the middle originated only from the \( +\frac{1}{2} \) to \(-\frac{1}{2} \) transition, the pulse width should be narrower by a factor of 2. These findings indicate that we are observing a superposition of the \( +\frac{1}{2} \) to \(-\frac{1}{2} \) and \( \pm\frac{3}{2} \) transitions in all cases, which would lead to a single exponential recovery curve for the spin-lattice relaxation process. Since our sample is an alloy-doped with Mn\(^{2+} \) magnetic moments, however, \( \frac{1}{T_1} \) is bound to have a distribution. We therefore use a stretched exponential function to fit the \( T_1 \) recovery data in all cases (see Supplemental Materials)\(^2\(^2\). This is a standard practice for NMR studies of inherently disordered magnetic materials.

We summarize the results of \( \frac{1}{T_1} \) in Fig. 4. The nuclear spin-lattice relaxation time \( T_1 \) represents the time scale during which Li nuclear spins relax to their thermal equilibrium after the absorption of radio frequency pulses. \( \frac{1}{T_1} \) becomes larger when more low energy spin excitations associated with the Mn spins or the conduction electrons exist. Theoretically, the spin contribution to \( \frac{1}{T_1} \) may be written using the imaginary part of the dynamical electron spin susceptibility \( \chi''(\mathbf{q},\omega) \) as \( \frac{1}{T_1} \propto \sum_{\mathbf{q}} |A(\mathbf{q})|^2 \chi''(\mathbf{q},\omega) \, \chi''(\mathbf{q},\omega) \), where \( A(\mathbf{q}) \) is the hyperfine form factor\(^2\(^3\). In the parent compound LiZnP, \( \frac{1}{T_1} \) of the Li(0) sites is as slow as \( \sim 0.004 \text{ s}^{-1} \). Such very slow relaxation rates are typical for non-magnetic insula-

![FIG. 3: (Color online) The temperature dependence of the \(^7\)Li NMR Knight shifts, \( ^7K \), at the Li(Mn) sites (■). The sign of \( ^7K \) is reversed, to take into account the negative sign of the hyperfine coupling \( A_0 \). The horizontal line represents \( ^7K_{\text{orb}} = 0.05\% \). Also shown is the HHFW of Li(0) in LiZn0.9Mn0.1P (●). For comparison, we overlay the temperature dependence of the bulk dc-magnetization \( M \) at 4 Tesla measured with SQUID (solid curve, normalized at 4.2 K). Inset: the dc-magnetization \( M \) measured at \( B_{\text{ext}} = 100 \text{ Oe} \); \( M \) increases sharply below \( T_c = 25 \text{ K} \). Notice that this feature is suppressed at \( B_{\text{ext}} = 4 \text{ Tesla} \). Dashed lines mark \( T_c = 25 \text{ K} \).](image-url)
tors, and consistent with the fact that both Mn moments and conduction carriers are absent in the non-magnetic semiconductor LiZnP.

Upon Mn doping, the relaxation rate increases dramatically. $\frac{1}{T_1} \sim 400 \text{ s}^{-1}$ at the Li(Mn) site observed above $T_c$ is five orders of magnitude enhanced compared with the non-magnetic LiZnP. This finding provides evidence for the presence of strong, low-frequency Mn spin fluctuations in the paramagnetic state above $T_c$. The suppression of $\frac{1}{T_1}$ below $T_c$ indicates that these spin fluctuations are suppressed once ferromagnetic long-range order is established. The temperature independence of $\frac{1}{T_1}$ in the broad temperature range from 280 K down to $\sim 30$ K also implies that the Mn spin-spin correlations are in the so-called exchange narrowed regime, where the energy scale of the thermal disturbance ($k_B T$) is comparable to or greater than that of the typical Mn-Mn spin interaction $|J|$. Using the Gaussian approximation for the spin-spin correlation function, we can express $\frac{1}{T_1} = \sqrt{\frac{2\pi}{\omega_e}} S(S+1) (\frac{A_0}{k_B T})^2 \sim 400 \text{ s}^{-1}$, where $S \lesssim 5/2^9$ and $A_0 = -12 \text{ kOe}/\mu_B$ as determined from Fig. 3. Therefore we estimate the characteristic frequency of the Mn spin fluctuations as $\omega_e \sim 1.1 \times 10^{15} \text{ rad/s}$ in the paramagnetic state above $T_c$.

This large value of $\omega_e$ sets a strong constraint on the nature of Mn-Mn spin interactions. First, we recall that $\omega_e^2 = \frac{2}{3} z S(S+1) (\frac{A_0}{k_B T})^2$ within the Gaussian approximation, where $z$ is the number of Mn sites within the range of Mn-Mn interactions. Since the high temperature regime with a constant $1/T_1 \sim 400 \text{ sec}^{-1}$ extends to $\sim T_c$, the typical Mn-Mn spin interaction energy scale $|J|$ is at most $\sim 100$ K. This implies that the number of Mn sites within the range of Mn-Mn interactions is as large as $\sim 10^3$. While our estimation may be somewhat crude, our $1/T_1$ data establishes that each Mn spin interacts with a very large number of other Mn spins, rather than just a few Mn sites in the immediate vicinity. Our finding is consistent with the earlier theoretical proposal that the Mn-Mn spin interactions are caused primarily by the long-range interactions, such as the p-d Zener exchange interaction mediated by conduction carriers (doped holes or electrons), which is the semiconductor analogue of the RKKY interaction in metals. We note, however, that our finding based on $\omega_e$ only implies the extended nature of the Mn-Mn interactions, and does not rule out other interaction mechanisms.

$\frac{1}{T_1}$ at the main Li(0) peak of LiZn$_{0.9}$Mn$_{0.1}$P is slower than the Li(Mn) site by a factor of $\sim 50$. This is consistent with the fact that Li(0) sites do not have Mn at their n.n. sites, hence the effects of Mn spin fluctuations are much more limited due to weaker hyperfine couplings. Nonetheless, $\frac{1}{T_1}$ at the Li(0) peak also exhibits a kink around $T_c$, indicating that Li(0) sites are indeed under the influence of ferromagnetic Mn spin fluctuations as well. The observed linear increase of $\frac{1}{T_1} \sim a + b T$ above $T_c$ suggests that Li(0) nuclear spins may have two separate relaxation mechanisms. The constant a-term is caused by Mn spin fluctuations, in analogy with the constant behavior observed for Li(Mn), while the small T-linear b-term may be attributed to the Korringa process arising from the Fermi surface excitations of a small number of conduction carriers. This carrier might also facilitate the interactions between distant Mn sites.

To summarize, the successful synthesis of the bulk form of I-II-V DMS, LiZn$_{0.9}$Mn$_{0.1}$P with $T_c = 25$ K, enabled us to investigate the nature of its ferromagnetism by microscopic $^7$Li NMR techniques. In particular, by successfully identifying the $^7$Li NMR signals arising from the Li sites n.n. to the Mn spins, we were able to probe the static and dynamic magnetic susceptibility of Mn spins through the NMR Knight shift and $1/T_1$. We deduced the characteristic Mn spin fluctuation frequency $\omega_e$, and showed that the Mn-Mn spin interaction extends many unit cells. Regardless of the exact mechanism of such interactions, our findings explain why DMS could exhibit a relatively high $T_c$ with a low density of Mn.

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