\textbf{\mu SR Investigation and Suppression of $T_C$ by overdoped Li in Diluted Ferromagnetic Semiconductor Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P}\\

Huiyuan Man$^1$, Xin Gong$^1$, Guoxiang Zhai$^1$, Shengli Guo$^1$, Cui Ding$^1$, Quan Wang$^1$, T. Goko$^{2,3}$, L. Liu$^2$, B. A. Frandsen$^4$, Y. J. Uemura$^2$, H. Luetkens$^5$, E. Morenzoni$^6$, C.Q. Jin$^1$, T. Munsch$^5$, G.M. Luke$^{5,6}$, Hangdong Wang$^7$, Bin Chen$^1$ and F. L. Ning$^1$\footnote{$^1$Department of Physics, Zhejiang University, Hangzhou 310027, China \ $^2$Department of Physics, Columbia University, New York, New York 10027, USA \ $^3$Paul Scherrer Institute, Laboratory for Muon Spin Spectroscopy, CH-5232 Villigen PSI, Switzerland \ $^4$Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China \ $^5$Department of Physics and Astronomy, McMaster University, Hamilton, Ontario L8S4M1, Canada \ $^6$Canadian Institute for Advanced Research, Toronto, Ontario M5G1Z8, Canada and \ $^7$Department of Physics, Hangzhou Normal University, Hangzhou 310016, China (Dated: June 17, 2014)\\

We use muon spin relaxation ($\mu$SR) to investigate the magnetic properties of a bulk form diluted ferromagnetic semiconductor (DFS) Li$_{1.15}$(Zn$_{0.8}$Mn$_{0.2}$)P with $T_C \sim 22$ K. $\mu$SR results confirm the gradual development of ferromagnetic ordering below $T_C$ with a nearly 100% magnetic ordered volume. Despite its low carrier density, the relation between static internal field and Curie temperature observed for Li(Zn,Mn)P is consistent with the trend found in (Ga,Mn)As and other bulk DFSs, indicating these systems share a common mechanism for the ferromagnetic exchange interaction. Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P has the advantage of decoupled carrier and spin doping, where Mn$^{2+}$ substitution for Zn$^{2+}$ introduces spins and Mn$^{3+}$ off-stoichiometry provides carriers. This advantage enables us to investigate the influence of overdoped Li on the ferromagnetic ordered state. Overdoping Li suppresses both $T_C$ and saturation moments for a certain amount of spins, which indicates that more carriers are detrimental to the ferromagnetic exchange interaction, and that a delicate balance between charge and spin densities is required to achieve highest $T_C$.\\
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\section{INTRODUCTION}\\

The successful fabrication of III-V (In,Mn)As and (Ga,Mn)As through low temperature molecular beam epitaxy (LT-MBE) has generated extensive research into diluted ferromagnetic semiconductors (DFS)\cite{1,2}. Theoretically, it has been proposed that $T_C$ can reach room temperature with sufficient spin and carrier density\cite{2}. After almost two decades’ efforts, the Curie temperature $T_C$ of (Ga,Mn)As thin films has been improved to as high as 200 K\cite{3,4}. One of the major intrinsic difficulties is the low solubility of Mn$^{2+}$ substitution for Ga$^{3+}$, which makes it difficult to enhance the concentration of Mn while controlling the homogeneity of thin films. Mn$^{2+}$ substitution for Ga$^{3+}$ provides not only local moments but also hole carriers. During the fabrication of thin films, some Mn$^{2+}$ easily get into the interstitial sites and become a double donor, which makes it difficult to determine precisely the amount of Mn that substitutes for Ga at the ionic sites\cite{5}. Investigating some DFS systems with more controllable spin and carrier density might be helpful in understanding the general mechanism of ferromagnetism.

Recently, several bulk form DFS families that are derivatives of FeAs-based high temperature superconductors have been reported\cite{6,7}. Among them, the $T_C$ of 122 type bulk form (Ba,K)(Zn,Mn)$_2$As$_2$ reaches $\sim 180$ K,\cite{6} which is already comparable with the record $T_C$ of (GaMn)As\cite{8,9}. $\mu$SR measurements have shown that the relation between static internal field and Curie temperature observed in I-III-V Li(Zn,Mn)As\cite{10} 1111 type (La,Ba)(Zn,Mn)AsO\cite{11} and 122 type (Ba,K)(Zn,Mn)$_2$As$_2$\cite{12} DFSs all fall into the scaling observed in (Ga,Mn)As thin films\cite{13} indicating they all share a common mechanism for the ferromagnetic exchange interaction. The availability of a specimen in bulk form also enables the NMR measurements of DFS. Through $^7$Li NMR of Li(Zn,Mn)P,\cite{13} Ding et al. successfully identified Li(Mn) sites that have Mn$^{2+}$ at N.N. (nearest neighbor) sites, and found that the spin lattice relaxation rate $1/\tau_{\text{L}}$ is temperature independent above $T_C$, i.e., $1/\tau_{\text{L}} \sim 400$ s$^{-1}$, indicating that Mn spin-spin interaction extends over many unit cells with an interaction energy $|J| \sim 100$ K.\cite{13} This explains why DFS exhibits a relatively high $T_C$ with such a low density of Mn.

The other advantage of these new bulk DFSs is the decoupling of carrier and spin doping. (La,Ba)(Zn,Mn)AsO DFS with $T_C \sim 40$ K\cite{14} for example, is achieved by doping Mn$^{2+}$ and Ba$^{2+}$ into the direct gap semiconductor LaZnAsO, where Mn$^{2+}$ substitution for Zn$^{2+}$ and Ba$^{2+}$ substitution for La$^{3+}$ introduce spin and hole carriers, respectively. Both Mn and Ba are chemically stable elements, and the concentrations of charge and spin can be precisely controlled. Very recently, by controlling the Li concentration and by doping Mn into the direct gap semiconductor LiZnP (gap $\sim 2.1$ eV)\cite{15,16} Li(Zn,Mn)P\cite{16} has
been found to experience a transition into ferromagnetic state below $\sim 34K$ with a low carrier density of $10^{16}/\text{cm}^3$. This carrier density is $\sim 3$ orders smaller than that of (Ga,Mn)As, Li(Zn,Mn)As and (Ba,K)(Zn,Mn)$_2$As$_2$, leaving the open questions about the mechanism behind ferromagnetism of Li(Zn,Mn)P.

In this paper, we use $\mu$SR to investigate the ferromagnetism of a I-II-V DFS Li(Zn,Mn)P with $T_C = 22$ K. Our $\mu$SR results demonstrate that a nearly 100% ferromagnetic ordered volume develops below $T_C$, indicating the homogenous distribution of Mn$^{2+}$ atoms. This result is consistent with NMR measurements of the same specimen. We also investigated the spin dynamics of Mn spins, and found that Li(Zn,Mn)P also falls into the same scalings of internal field and $T_C$ observed for (Ga,Mn)As and other bulk DFSs, indicating that Li(Zn,Mn)P belongs to the DFS families that share a common mechanism of ferromagnetic exchange interaction despite its much lower carrier density. Furthermore, taking advantage of decoupled carrier and spin doping, we studied the carrier doping effect on the ferromagnetic ordered state. Our experimental results show that overdoping Li suppresses both $T_C$ and the saturation moments. In other words, too many carriers are harmful to the development of ferromagnetic ordering in a similar way as too few.

II. EXPERIMENTS

The Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P polycrystalline specimens 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 $^\circ$C in evacuated silica tubes, and held at 450 $^\circ$C for 48 hours. After cooling down to room temperature, the mixture was ground thoroughly, then pressed into pellets and heated again to ensure the complete reaction. The handling of materials was performed in a high-purity argon filled glove box (the percentage of O$_2$ was $\leq 0.1$ ppm) to protect it from air. Powder X-ray diffraction was performed at room temperature using a PANalytical X-ray diffractometer (Model EMPYREAN) with monochromatic CuK$_{\alpha 1}$ radiation. The dc magnetization measurements were conducted on Quantum Design SQUID (superconducting quantum interference device). Zero-field (ZF) and weak-transverse-field (WTF) muon spin relaxation measurements were performed at PSI and TRIUMF. The specimen used for $\mu$SR study in this work is the same piece as used in the NMR study.24
Asymmetry

FIG. 3: (Color online) $\mu$SR time spectra of Li$_{1.15}$(Zn$_{0.9}$Mn$_{0.1}$)P in a weak-transverse-field of 30 Oe. The oscillation amplitude corresponds to the paramagnetic volume faction.

III. RESULTS AND DISCUSSION

In Fig 1(a), we show powder X-ray diffraction patterns of the parent compound LiZnP with the Miller indices. Bragg peaks can be well indexed into a cubic structure with a space group $\overline{F}43m$, identical to the zinc blende GaAs.$^{13,14}$ Doping excess Li and Mn into the parent compound does not change the crystal structure and no impurities have been observed. The lattice constants $a$ of Li$_{1+y}$(Zn$_{0.93}$Mn$_{0.07}$)P and Li$_{1+y}$(Zn$_{0.9}$Mn$_{0.1}$)P are shown in Fig. 1(b). The evolution of lattice constant $a$ follows the Vegard law, indicating the successful Li doping. This trend can also be seen from the amplified (111) peaks shown in Fig. 1(c) and (d), which shift systematically towards smaller $2\theta$ with increasing $y$, suggesting that Li atoms are indeed incorporated into the lattice. This results in the enlargement of the unit cell. In addition, it has been shown that the NMR line width of LiZnP is only $\sim 4$ KHz.$^{24}$ This is comparable to the line width of pure Cu metal, indicating the high quality of these polycrystals. We do not observe signals arising from Li atoms that enter Zn sites which would give rise to additional NMR peaks due to the different electrical environment they are located in.$^{24}$

In Fig. 2, we show the time spectra of the

Zero-field (ZF) $\mu$SR on the polycrystalline sample Li$_{1.15}$(Zn$_{0.9}$Mn$_{0.1}$)P which has a $T_C = 22$ K. It can be seen that the time spectra clearly displays an increase in relaxation rate below $T = 15$ K. We note that no clear oscillation is observed even at 2 K; a similar situation is observed in (Ga,Mn)As$^{23}$ and Li(Zn,Mn)As$^{13}$ as well. This can be attributed to the random distribution of Mn moments in real space because Mn substitution for Zn is random. This makes the local field at the muon site highly random even in the ferromagnetic ground state, and ZF precession signals are subsequently strongly damped. The random distribution of Mn moments has also been shown by Li(Mn) NMR lineshapes, which displays a large distribution between 61 MHz and 66 MHz.$^{24}$ The broad NMR line arises from the distribution of hyperfine fields at Li(Mn) sites, which can be as large as $\sim 0.3$ Tesla.$^{24}$ Note that the transferred hyperfine coupling between Li nuclear spins and Mn electrons is much weaker than those between Zn/Mn and As. Currently, we do not know the exact muon sites in Li(Zn,Mn)P, but relatively large hyperfine fields at muon sites are likely. We employed a two component function to analyze the ZF spectra (the fitting function is identical to the one used for Li(Zn,Mn)As, as explained in the method section of ref. 13). One component is for a static magnetic field with a Lorentzian distribution. This is expected for dilute Mn moments randomly substituting Zn sites, representing the magnetically ordered volume. The other component is an exponential function, representing the volume fraction of fluctuating paramagnetism. The derived ferromagnetic ordered volume fraction is shown in Fig. 4.

In Fig. 3, we show the $\mu$SR time spectra measured in a weak transverse field (WTF) of 30 Oe. As stated
TABLE I: Curie temperature ($T_C$), Weiss temperature ($\theta$), the effective moment ($M_{eff}$), and the saturation moment ($M_{sat}$), the value measured at $T = 5$ K and $H = 500$ Oe for Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P.

| $y$ (excess Li) | $T_C$ (K) | $\theta$ (K) | $M_{sat}$ ($\mu_B$/Mn) | $M_{eff}$ ($\mu_B$/Mn) | Coercivity (Oe) |
|----------------|-----------|--------------|------------------------|------------------------|----------------|
| Li$_{1+y}$(Zn$_{0.93}$Mn$_{0.07}$)P | 0.07 | 25 | 24.5 | 0.61 | 3.40 | 20 |
| | 0.10 | 24 | 23.0 | 0.32 | 2.40 | 16 |
| | 0.15 | 24 | 23.0 | 0.37 | 2.02 | 25 |
| Li$_{1+y}$(Zn$_{0.93}$Mn$_{0.1}$)P | 0.07 | 22 | 23.4 | 0.19 | 1.94 | 24 |
| | 0.10 | 25 | 23.4 | 0.41 | 2.52 | 14 |
| | 0.12 | 22 | 18.4 | 0.23 | 2.34 | 20 |
| | 0.15 | 22 | 17.7 | 0.22 | 2.29 | 20 |

![Graph](image_url)
$1/M \sim T$, see ref. 14), and $M(H)$ has a parallelogram shape with a coercive field of $\sim 20$ Oe. Another feature of the Li$_{1+y}$(Zn$_{0.93}$Mn$_{0.07}$)P specimen is that ZFC and FC curves display a bifurcation shortly below $T_C$. We fitted the $M(T)$ curve above $T_C$ according to the Curie-Weiss law, $\chi - \chi_0 = C/(T - \theta)$, where $C$ is Curie constant and $\theta$ the Weiss temperature, and derived the effective paramagnetic moment, $M_{eff}$, from the Curie constant $C$. $M_{eff}$ is $\sim 3\mu_B/M_n$ for $y = 0.07$. This value is smaller than $4.5 \mu_B/M_n$ of Li$_{1+y}$(Zn$_{0.97}$Mn$_{0.03}$)P in ref. 14. $M_{eff} \sim 5-6 \mu_B/M_n$ is expected for high state Mn$^{2+}$ ions. Apparently, the suppression of $M_{eff}$ is not only arising from the competition of the antiferromagnetic exchange interaction of N.N. Mn$^{2+}$, but also from the overdoped carriers, as will be shown in detail in the following.
We plot Curie temperature ($T_C$), Weiss temperature ($\theta$), the effective moment ($M_{eff}$), and the saturation moment ($M_{sat}$), the value measured at $T = 5$ K and H = 500 Oe) versus the nominal excess Li concentration in Fig. 6(c). For Li concentration equal to 1 (i.e., $y = 0$), Li(Zn$_{0.93}$Mn$_{0.07}$)P remains a paramagnetic ground state. We therefore define $T_C$, $\theta$, $M_{eff}$ and $M_{sat}$ as zero, and plot zero in Fig. 6(c) for comparison. Clearly, we can see that all four parameters display qualitatively similar Li concentration dependence. They increase with Li concentration initially, reach a maximum at $y = 0.07$, and then start to decrease when overdoped with Li. To examine if the same trend is valid in a different Mn concentration, we also investigate these parameters in Li$_{1+y}$(Zn$_{0.9}$Mn$_{0.1}$)P ($x = 0.10$ and $y = 0.07, 0.10, 0.12$ and 0.15), and show the results in Fig. 7. The situation is similar to the case of the x = 0.07 specimens. $T_C$, $\theta$, $M_{sat}$, and $M_{eff}$ first increase from $y = 0$ to $y = 0.07$, reach a maximum at $y = 0.10$, and then decrease from $y = 0.10$ to $y = 0.15$ for Li$_{1+y}$(Zn$_{0.9}$Mn$_{0.1}$)P. We tabulate all these parameters in Table 1.

It has been theoretically proposed that in diluted magnetic semiconductors, spins are mediated by hole carriers through RKKY interaction. From NMR measurements of Li$_{1+y}$(Zn$_{0.9}$Mn$_{0.1}$)P, it has been shown that the spin lattice relaxation rate $1/T_1$ of Li(0) sites, where zero means no Mn at N.N. Zn sites for Li, display a Korringa behavior, i.e., Fermi surface excitations of a small number of conduction carriers. The $1/T_1$ of Li(Mn) site shows a T-independent behavior caused by spin fluctuations, i.e., representing local moments. This provides direct and convincing experimental evidence that Fermi degenerate conduction carriers mediate the Mn-Mn spin interactions through the p-d exchange interaction, and that the Mn-Mn spin interaction is long-ranged, rather than a nearest-neighbor exchange interactions. The RKKY exchange interaction can be written as, $J \sim \cos(2k_F r)/r^2$, where $k_F$ is the radius of Fermi surface (assuming the Fermi surface is a spherical shape) and $r$ the distance between two localized moments. The first oscillation period of the RKKY interaction supports ferromagnetic coupling. In our case, doping more Li introduces more carrier, and subsequently modifies the density of states and, therefore, the shape of Fermi surface. The modified Fermi surface affects the period of oscillation, as well as the ferromagnetic ordering.

IV. CONCLUSION

We conducted $\mu$SR investigation of a bulk form I-II-V DFS Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P. Our $\mu$SR results confirm the development of ferromagnetic ordering below $T_C$ with a nearly 100% magnetically ordered volume. Despite its much lower carrier density, Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P shares a common mechanism for the ferromagnetic exchange interaction with (Ga,Mn)As, Li(Zn,Mn)As, 1111 type (La,Ba)(Zn,Mn)AsO and 122 type (Ba,K)(Zn,Mn)$_2$As$_2$. Taking advantage of the decoupled nature of the carrier and spin doping in Li$_{1+y}$(Zn$_{1-x}$Mn$_x$)P, we investigated, for the first time, the influence of overdoped carriers on the ferromagnetic ordered state of a DFS. We found that overdoped Li suppresses both $T_C$ and magnetic moments. A simple explanation is the modification of the Fermi surface caused by extra carriers. More detailed theoretical models are expected to explain this phenomena.

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