Diluted ferromagnetic semiconductor Li(Zn,Mn)P with decoupled charge and spin doping


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We report the discovery of a diluted magnetic semiconductor, Li(Zn,Mn)P, in which charge and spin degrees of freedom are decoupled. Utilizing charge carrier mobility, we were able to independently control the concentration of holes and electrons in Li(Zn,Mn)P. The system remains magnetic over a wide range of carrier concentrations. The critical temperature, Curie temperature, and Curie-Weiss temperature of Li(Zn,Mn)P were found to be 28 K, 29 K, and 26 K, respectively. These values are comparable to those for Li(Zn,Mn)As and (Ga,Mn)As, which are 25 K, 24 K, and 18 K, respectively. These results suggest that Li(Zn,Mn)P is a promising candidate for spintronics applications.

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I. INTRODUCTION

Spintronic devices utilize the electron’s charge and spin degrees of freedom to achieve novel quantum functionalities. Diluted magnetic semiconductors (DMS) constitute an important category of spintronic materials that have the potential to be successfully incorporated into the existing semiconductor industry. The prototypical DMS (Ga,Mn)As, discovered in the 1990s, accomplishes spin and charge doping simultaneously through the heterovalent substitution of Mn+2 for Zn+2, respectively. Isostructural to (Ga,Mn)As, Li(Zn,Mn)P was found to be a p-type ferromagnetic semiconductor with excess lithium providing charge doping. First-principles calculations indicate that excess Li is favored to partially occupy the Zn site, leading to hole doping. Ferromagnetism with Curie temperature up to 34 K is achieved while the system still shows semiconducting transport behavior.

II. EXPERIMENT

Polycrystalline specimens were prepared as described in Refs. 2 and 3. High-purity starting materials with molar amounts proportional to the nominal element concentrations were pressed into a pellet and loaded into a Ta tube with high-purity argon. The Ta tube, which prevents the evaporation of Li, was then sealed into an evacuated quartz tube. All procedures were performed in a glove box under high-purity argon atmosphere. The specimens were heated to 900 °C and held for several days before the temperature was slowly decreased. The specimens were characterized by x-ray powder diffraction on a PANalytical X’Pert diffractometer operating with Cu Kα radiation. Lattice parameters were determined via Rietveld analysis using the GSAS software package. The real atomic ratios of heavy elements such as Zn, Mn, or As measured from energy dispersive analysis of x-ray (EDAX) are nearly the same as the nominal ones, such as those for Mn(Zn + Mn), which are about 0.032, 0.051, and 0.074 for Li1.02(Zn0.97Mn0.03)P, Li1.02(Zn0.95Mn0.05)P, and Li1.02(Zn0.93Mn0.07)P, respectively. It is rather difficult to measure Li concentration since it is a very light element. But its concentration evolution can be inferred from lattice parameter change. Successful Li and Mn doping are supported by continuing lattice constant increasing as shown in Fig. 1(b). The concentrations of Li and Mn in the paper therefore use the nominal composition.
FIG. 1. (Color online) (a) Crystal structure of LiZnP showing [ZnP₄] tetrahedral coordination. (b) Lattice constants of Li₁₋ₓZn₁−ₓMnₓP, Li₁₋₀₂Zn₁−ₓMnₓP, and Li₁₋₀₄Zn₁−ₓMnₓP for various Li and Mn concentrations. The systematic change of lattice parameters indicates the successful substitution of the elements.

Magnetometer (SQUID-VSM). Resistivity and Hall effect measurements were carried out on a Quantum Design Physical Property Measurement System (PPMS) using the four-probe method and the Hall bar method, respectively.

III. RESULTS AND DISCUSSION

A. Experimental results

Step-scanning powder x-ray diffraction measurements showed that pristine LiZnP crystallizes into a structure similar to zinc-blende-type GaAs with space group $F\overline{4}3m$ as shown in Fig. 1(a). The refined lattice parameter of LiZnP is $a = 5.7564$ Å.⁹,¹⁰ We found that chemically stable bulk crystals of Li₁₊ₓ(Zn₁−ₓMnₓ)P can be obtained for excess Li with $y \leq 0.15$ and Mn concentrations $x$ up to at least 0.1. As shown in Fig. 1(b), the lattice parameter evolved systematically with Li and Mn concentrations, suggesting successful chemical doping.

The temperature-dependent magnetization $M(T)$ and field-dependent magnetization $M(H)$ were measured for Li₁₋ₓ(Zn₁−ₓMnₓ)P with $-0.05 \leq y \leq 0.07$ and $x = 0$, 0.03, 0.06, and 0.1. The specimens with deficient Li showed spurious weak ferromagnetic signals above room temperature caused by the ferromagnetic impurity MnP.¹¹ Specimens with excess Li, on the other hand, demonstrated robust ferromagnetism, as displayed in Fig. 2. Figure 2(a) shows $M(T)$ for Li₁₋₀₄(Zn₁−ₓMnₓ)P specimens, $x = 0$, 0.03, 0.06, and 0.1, in an applied field of 100 Oe in both zero-field-cooling (ZFC) and field-cooling (FC) modes. $T_C$, determined by the projected line method, clearly increases up to 34 K, as shown in Fig. 2(b). Above $T_C$, the susceptibility $\chi$ can be fit to Curie-Weiss law [Figs. 2(a) and 2(b)], 

$$\left(\chi - \chi_0\right)^{-1} = \left(T - \theta\right)/C,$$

where $\chi_0$ is a temperature-independent term, $C$ is the Curie constant, and $\theta$ is the Weiss temperature. The positive value of $\theta$ found for Li₁₋₀₄(Zn₁−ₓMnₓ)P [Fig. 2(b)] indicates a ferromagnetic interaction between Mn²⁺ ions.

The effective paramagnetic moment ($M_{\text{eff}}$) obtained from the Curie constant [solid purple circles in Fig. 2(b)] decreases with increasing Mn doping, a trend also found in other systems doped with magnetic ions.¹²-¹⁴ Extrapolation of $M_{\text{eff}}$...
to lower Mn concentrations yields a value of approximately 5.9μB/Mn, as expected for the fully high-spin oriented Mn^{2+} ion. Figure 2(b) also shows the saturation moment per Mn (M_{sat}) in an applied field of 500 Oe, found to be about 1–2μB/Mn. For ferromagnetic (Ga,Mn)As, Li(Zn,Mn)As, and (Ba,K)(Zn,Mn)\textsubscript{2}As\textsubscript{2}, M_{sat} are about 2–4μB/Mn,\textsuperscript{15} 1–3μB/Mn,\textsuperscript{1} and 1–2μB/Mn,\textsuperscript{3} respectively, which are comparable to that of Li(Zn,Mn)P. As M_{eff}, M_{sat} decreases with increasing Mn concentration, likely due to competition between antiferromagnetic coupling of nearest neighbor Mn moments and ferromagnetic coupling of Mn moments mediated by the doped hole carriers. Figure 2(c) shows the hysteresis curves for Li_{1.04}Zn_{0.9}Mn_{0.1}P, indicating soft ferromagnetic behavior with a very small coercive field (H_{C}) of ~50 Oe.

LiZnP was reported to be a semiconductor with a direct band gap around 2.04 eV.\textsuperscript{9} Figure 3(a) shows the resistivity and carrier concentration of Li_{1.04}Zn_{0.9}Mn_{0.1}P from 5–300 K. The resistivity value was diverging and too large at low temperature. Any small misalignment of the two Hall contacts would pick up a longitudinal resistivity signal and this brought large trouble in the Hall effect measurement. As shown in the inset of Fig. 3(a), even a 100 K Hall curve became difficult for measurement. Therefore no anomalous Hall effect signal was detected so far because of technical problems. However, Hall effect measurement of relative high temperature already told us the carrier type and concentration. The conclusion that ferromagnetic order was achieved while the system still shows semiconducting transport behavior is what we can present in this Rapid Communication. Nevertheless, this Rapid Communication just reports the first step of the DMS material. A higher quality sample such as single crystal and high-quality epitaxial film which we are working on will solve the problem.

As plotted in Fig. 3(a), the resistivity obviously increases with decreasing temperature, whereas the mobile hole concentration decreases. This is indicative of typical semiconducting behavior. Somewhat surprisingly, Li_{1+x}(Zn,Mn)P, 0 < x < 0.7, is found to exhibit p-type behavior, not the n-type behavior that one would expect assuming that excess Li provides additional electrons. This is explained by first-principles calculations, which indicate that the excess Li\textsuperscript{+} ions are thermodynamically favored to occupy the Zn\textsuperscript{2+} sites (see the following section), thereby rendering Li(Zn,Mn)P a p-type DMS.

Previous studies of (Ga_{1-x},Mn)\textsubscript{x}As demonstrated that for 0.012 ≤ x ≤ 0.03, ferromagnetic order can be achieved in the full volume fraction while the system still shows semiconducting transport behavior,\textsuperscript{15} implying that the paramagnetic to ferromagnetic quantum transition occurs at a different charge/spin concentration than the semiconductor to metal quantum transition. The present work confirms the same situation for Li(Zn,Mn)P. The hole concentration calculated from Hall effect measurements of charge/spin codoped Li_{1.04}Zn_{0.9}Mn_{0.1}P [inset of Fig. 3(a)] is larger than that of pristine LiZnP by more than a factor of 10, but still results in semiconducting transport behavior.\textsuperscript{9} Nonetheless, this small hole concentration is evidently sufficient to mediate ferromagnetic coupling of the dilute Mn moments and induce magnetic order. It is likely that the doped holes are not fully delocalized but have sufficient spread in real space to mediate magnetic coupling between neighboring Mn spins, thereby facilitating the buildup of a percolating magnetic network.

Figure 3(b) compares the hole concentrations and ferromagnetic transition temperatures of Li(Zn,Mn)P to those of other DMS systems. The hole concentration of Li_{1.04}Zn_{0.9}Mn_{0.1}P is more than two orders of magnitude smaller than that of typical metallic DMS ferromagnets.\textsuperscript{2,3,14,16,17} The relationship between hole concentration and T_{C} exhibited by the other systems suggests that further charge and spin doping would
TABLE I. Formation energy for excess Li atom at different sites, obtained by DFT calculations. By Ref. 25, the formation energy is given by $E_{\text{formation}} = E_T - n_L(\mu_{Li}) - n_{Zn}(\mu_{Zn}) - n_P(\mu_{P})$, where $E_T$ is the total energy of the supercell, $n_x$ is the number of $x$ atoms in the supercell, and $\mu_x$ is the atomic chemical potential. It has $\mu_{Li} + \mu_{Zn} + \mu_{P} = \mu_{LiZnP(black)}$. Table I shows formation energy for two extreme conditions, i.e., the Li-rich plus Zn-rich limits ($\mu_{Li} = \mu_{Li(bulk)}$, $\mu_{Zn} = \mu_{Zn(bulk)}$) and the Li-rich plus P-rich limit ($\mu_{Li} = \mu_{Li(bulk)}$, $\mu_{P} = \mu_{P(bulk,black)}$). The experimental condition can be between these two extreme conditions.

<table>
<thead>
<tr>
<th>LiZnP with excess Li</th>
<th>Formation energy (Li-rich and Zn-rich limits)</th>
<th>Formation energy (Li-rich and P-rich limits)</th>
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</thead>
<tbody>
<tr>
<td>Intersitial Li (supercell Li$<em>{28}$Zn$</em>{27}$P$_{27}$)</td>
<td>2.67 eV</td>
<td>2.67 eV</td>
</tr>
<tr>
<td>Li at Zn site and Zn is removed (supercell Li$<em>{28}$Zn$</em>{27}$P$_{27}$)</td>
<td>0.45 eV</td>
<td>$-0.93$ eV</td>
</tr>
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</table>

cause Li(Zn,Mn)P to become metallic and magnetically order at a higher $T_C$. We are currently working on optimizing the materials processing to show this behavior.

Magnetotransport measurements performed on Li$_{1.02}$Zn$_{0.98}$Mn$_{0.02}$P are shown in Fig. 3(c). Several types of effects can produce a magnetoresistance in magnetic semiconductors. Under many conditions, negative magnetoresistance results from the reduction of spin-dependent scattering by aligning the spins in the applied field. However, as shown in Figs. 2(c) and 3(c), the negative magnetoresistance is far from saturation in rather high magnetic field, in which spin orientation is fully aligned. In this condition, the negative magnetoresistance is presumably from the weak localization effects. No signature of a metal-insulator phase transition could be found at the Curie point. The resistivity $\rho$ increases monotonically with decreasing temperature, showing a rapid rise below $T_C$. Hysteresis is observed in $\rho(H)$ for low fields ($\sim$50 Oe) and low temperatures, corresponding closely to the behavior of the magnetization $M(H)$ [see Fig. 2(c)].

B. Theoretical analysis

We studied the electronic state in Li(Zn,Mn)P with excess Li. We found that (i) for the compound the excess Li atoms prefer to occupy Zn-substitutional sites Li$_{Zn}$, and thus create the $p$-type carriers; (ii) the ferromagnetic correlations between Mn ions develop for the case of $p$-type carriers, and the corresponding effective exchange constant is smaller in Li(Zn,Mn)P than that in Li(Zn,Mn)As and leads to lower Curie temperature.

To study the stable state for excess Li atoms in the Li(Zn,Mn)P compound, we calculated the electronic structures by using the density functional theory (DFT) implemented in the code QUANTUM ESPRESSO. The exchange-correlation interactions are described by the Perdew-Burke-Ernzerhof generalized gradients approximation (GGA), and the electron-ion interactions are represented by the Vanderbilt ultrasoft pseudopotentials. We calculate the formation energy for the interstitial site Li$_I$ and the Zn-substitutional site Li$_{Zn}$, respectively. Since Mn at Zn-substitutional site Mn$_{Zn}$ do not introduce any carriers, we study the excess Li in LiZnP. Excess Li atom at interstitial sites Li$_I$ contributes one electron, while Li$_{Zn}$ contributes one hole to the system. Our DFT calculations show that Li$_{Zn}$ makes the formation energy lower than the Li$_I$ case as shown in Table I. It means the carriers will be holes.

To study the magnetic correlations between Mn in Li(Zn,Mn)P, we take the two-step calculations by our combined DFT + QMC (quantum Monte Carlo) method. First, the one-particle parts of the Anderson impurity model are formulated within the DFT for determining the host band structure and the impurity-host hybridization. Second, the correlation parts of the Anderson impurity model at finite temperatures are calculated by the QMC method. The calculation details will be published elsewhere. In $p$-type Li(Zn,Mn)P, ferromagnetic correlations between Mn impurities are obtained by our QMC calculations. In addition, we find that the effective exchange coupling in Li(Zn,Mn)P is larger than that in Li(Zn,Mn)As. By simple molecular-field theory, larger $T_C$ is expected for larger exchange coupling. This may be the reason why a lower Curie temperature is obtained in Li(Zn,Mn)P than that in Li(Zn,Mn)As.

IV. CONCLUSIONS

In summary, a bulk diluted magnetic semiconductor Li(Zn,Mn)P was successfully synthesized with decoupled spin and charge doping. Li(Zn,Mn)P is a soft magnet with a relatively small coercive field. Ferromagnetic order arises with semiconducting transport behavior, indicating the potential to further enhance $T_C$ with more itinerant carriers. This new DMS will contribute to the further development of new semiconductor materials and spintronic devices based on the individual tuning of spin and charge.

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