

Dilute Moment n -Type Ferromagnetic Semiconductor Li(Zn,Mn)As

J. Mašek,¹ J. Kudrnovský,¹ F. Máca,¹ B. L. Gallagher,² R. P. Campion,² D. H. Gregory,³ and T. Jungwirth^{4,2}

¹*Institute of Physics ASCR, Na Slovance 2, 182 21 Praha 8, Czech Republic*

²*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*

³*Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, United Kingdom*

⁴*Institute of Physics ASCR, Cukrovarnická 10, 162 53 Praha 6, Czech Republic*

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We propose to replace Ga in (Ga,Mn)As with Li and Zn as a route to high Curie temperature, carrier mediated ferromagnetism in a dilute moment n -type semiconductor. Superior material characteristics, rendering Li(Zn,Mn)As a realistic candidate for such a system, include high solubility of the isovalent substitutional Mn impurity and carrier concentration controlled independently of Mn doping by adjusting Li-(Zn,Mn) stoichiometry. Our predictions are anchored by *ab initio* calculations and comparisons with the familiar and directly related (Ga,Mn)As, by the physical picture we provide for the exchange interaction between Mn local moments and electrons in the conduction band, and by analysis of prospects for the controlled growth of Li(Zn,Mn)As materials.

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(Ga,Mn)As is prototypical of a unique class of spintronic material in which ferromagnetic coupling between dilute local moments is mediated by semiconductor band carriers [1,2]. This unusual behavior is realized in the conventional semiconductor GaAs using only one type of dopant, Mn_{Ga} , which provides both local spins and holes. The simplicity of such a system inevitably brings also limitations to the structural, ferromagnetic, and semiconducting properties due to the low solubility of Mn and due to the lack of independent control of local moment and carrier densities. Among the negative consequences are Curie temperatures below room temperature and p -type conduction only. Here we predict that these limitations can be lifted by a straightforward substitution of the group-III Ga with group-I Li and group-II Zn.

LiZnAs is a stable direct-gap semiconductor which can be grown by the high-temperature reaction of elemental Li, Zn, and As [3,4]. Its crystal structure and band structure are very similar to those of GaAs. As shown in Figs. 1(a) and 1(b), the LiZnAs tetrahedral lattice can be viewed as a zinc blende ZnAs binary compound, analogous to GaAs, filled with Li atoms at tetrahedral interstitial sites near As. The relatively small first ionization energy of Li makes the $(\text{Li})^+(\text{ZnAs})^-$ compound half ionic and half covalent [5]. The measured band gap of LiZnAs (1.61 eV) is very similar to the GaAs band gap (1.52 eV) [6]. An overall similarity of the LiZnAs and GaAs electronic structures, including valence band and conduction band dispersions, ground state charge density, and phonon dispersion relations has been reported in *ab initio* local-density-approximation (LDA) studies [5,7].

Application of the LDA to magnetic properties of Mn-doped zinc blende semiconductors runs into a conceptual difficulty in dealing with local moment levels coincident with itinerant electron bands. To partly remedy this inadequacy we use in this Letter the LDA + U technique which

combines LDA with the Hubbard description of strongly correlated localized orbitals [8–11]. The LDA + U , with the Hubbard parameter $U = 3.5$ eV and the Hund's rule exchange parameter $J_H = 0.6$ eV, is implemented within the framework of the tight-binding linear muffin-tin orbital approach; impurity effects are accounted for using the coherent potential approximation (CPA) [12] which pro-

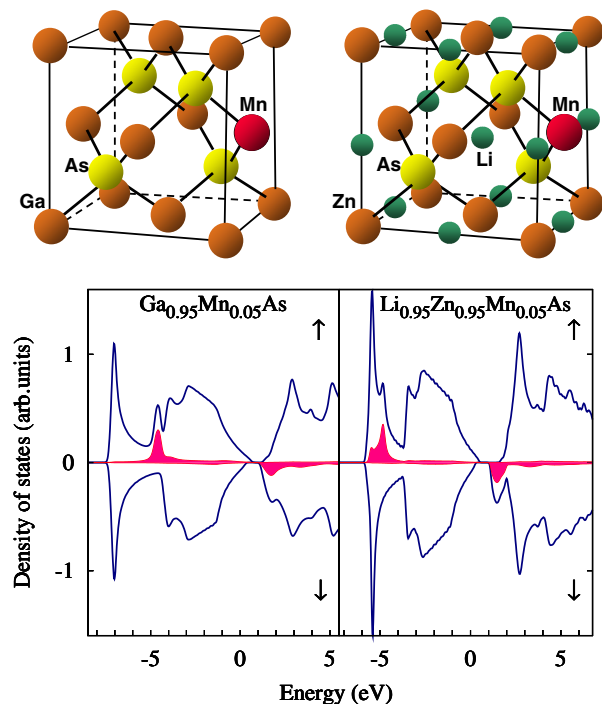


FIG. 1 (color online). Top panel: Schematics of (Ga,Mn)As and Li(Zn,Mn)As crystal structures. Bottom panel: *ab initio* total and Mn d -orbital projected density of states of $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$ and $\text{Li}_{0.95}\text{Zn}_{0.95}\text{Mn}_{0.05}\text{As}$ mixed crystals. Energy is measured from the Fermi energy.

vides configurational averaged spectral densities and band dispersions and is well suited for describing systems over a wide range of impurity concentrations [12]. We note that the qualitative study presented in this Letter is based on the systematic comparison of Li(Zn,Mn)As with the familiar (Ga,Mn)As and the conclusions we arrive at are independent of whether, e.g., LDA or LDA + U is applied. The similarity between LiZnAs and GaAs hosts allows us to relegate many of the important issues regarding applications of different *ab initio* approaches to the extensive literature on (Ga,Mn)As [2].

In Figs. 1(c) and 1(d) we compare LDA + U /CPA density of states (DOS) of LiZnAs and GaAs doped with 5% of Mn. Since Mn introduces one hole per Mn in GaAs but is isovalent in LiZnAs, the structure considered in Fig. 1(d) is $\text{Li}_{0.95}\text{(Zn}_{0.95}\text{Mn}_{0.05})\text{As}$ to allow for a direct comparison of *p*-type ferromagnets realized in the two hosts. As expected from the similar host band structures and nearly atomiclike character of Mn *d* states in (moderately) narrow-gap zinc blende semiconductors [13], both systems are ferromagnetic with comparable valence-band exchange splittings and similar Mn *d* and host *sp*-projected DOSs. In particular, the main peak in the majority-spin *d*-orbital DOS is well below the valence-band edge resulting in states near the Fermi energy having a predominantly As *p* character in both systems.

We now use the *ab initio* band structures to explore Li(Zn,Mn)As over a wide range of local moment and carrier dopings, including regimes which are technologically inaccessible in the GaAs host. We focus on the equilibrium solubility of isovalent Mn in LiZnAs for concentrations well above 1% and on ferromagnetism in LiZnAs with *n*-type conduction which, as we show, can be readily achieved without introducing additional chemical elements.

The formation energies of Mn_{Zn} are plotted in Fig. 2(a) for insulating stoichiometric Li(Zn,Mn)As, for *p*-type Li(Zn,Mn)As with Li vacancies, and for *n*-type Li(Zn,Mn)As with additional Li_I atoms occupying tetrahedral interstitial sites near Zn. (In the spirit of the previous literature on impurity formation energies in (Ga,Mn)As [14], we present here formation energy calculations based on the LDA.) Independent of the charge doping, the formation energy of Mn_{Zn} is negative; i.e., we find no equilibrium solubility limit for substitutional Mn_{Zn} , consistent with its isovalent nature. This result contrasts with the positive formation energy of Mn_{Ga} in GaAs [14] which leads to an equilibrium solubility limit below 1%. Note that our prediction for structurally stable Li(Zn,Mn)As compounds, derived from the LiZnAs host, with much larger Mn content is supported by the compatible tetrahedral crystal structure and semiconducting band structure of the existing LiMnAs ternary material [15,16]. (LiMnAs is an antiferromagnet [16] due to short-range Mn-Mn superexchange and therefore our study of ferromagnetic

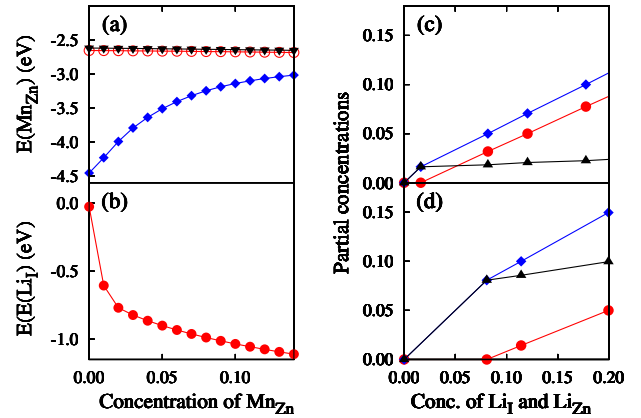


FIG. 2 (color online). (a) Mn_{Zn} formation energy in Li(Zn,Mn)As as a function of Mn_{Zn} doping for stoichiometric structures (red open circles), for *p*-type systems with 5% of Li vacancy acceptors (black triangles), and for *n*-type systems with 5% of donor Li_I impurities occupying Zn-tetrahedral interstitial sites (blue diamonds). (b) Li_I formation energy near the stoichiometric composition as a function of Mn_{Zn} doping. (c) Partial concentration of Li_I (blue diamonds) donors, Li_{Zn} acceptors (red circles), and net electron doping (black triangles) for 5% of Mn_{Zn} as a function of total concentration of excess Li (Li_I plus Li_{Zn}). (d) Same as (c) for 12.5% of Mn_{Zn} .

dilute Mn systems considers Mn concentrations still far from the LiMnAs limit.)

A detailed analysis of nonstoichiometric *n*-type Li(Zn,Mn)As is presented in Figs. 2(b)–2(d). Panel (b) demonstrates that in systems with over-stoichiometric Li concentrations a large number of Li_I atoms can be incorporated at interstitial sites near Zn. Formation energy of these single-donor impurities is negative and decreases with increasing Mn doping. In covalent semiconductors, carrier doping is limited due to a strong tendency to self-compensation, i.e., due to a spontaneous formation of defects preventing the Fermi energy from moving far into the band. In the LiZnAs host with excess Li, Li_{Zn} antisites represent natural single-acceptor compensating defects to the interstitial Li_I donors. *Ab initio* calculations of formation energies can be used [14,17] to estimate the dependence of Li_I and Li_{Zn} partial concentrations on the total density of excess Li atoms above the Li-(Zn,Mn) stoichiometry. Results are plotted in Figs. 2(c) and 2(d) for Mn doping of 5% and 12.5%. Although the tendency to self-compensation is clearly apparent, the theoretical data suggest that large net electron densities are feasible in Li(Zn,Mn)As owing to the partly ionic character of the compound. Remarkably, the *n*-type doping efficiency by excess Li increases significantly with increasing Mn concentration.

We now consider the magnetic properties of Li(Zn,Mn)As semiconductors. The compatibility of the CPA with Weiss mean-field theory allows us to estimate the strength of Mn-Mn coupling, at a given chemical composition, from the calculated energy cost E_{rev} of re-

versing one Mn moment with all other Mn moments aligned [18,19]. Results for E_{rev} shown in Fig. 3(a) were obtained using a rigid-band approximation. Here the LDA + U /CPA band structure was calculated in one charge state of the compound only, and the dependence on carrier doping was obtained by shifting the Fermi energy while keeping the bands fixed. Note that for the 5% Mn doping considered in the figure, carrier doping of $\pm 5\%$ corresponds to one electron or hole per Mn. Open and closed squares represent E_{rev} obtained applying the above rigid-band scheme, based on n -type $\text{Li}_{0.95}(\text{Zn}_{0.95}, \text{Mn}_{0.05})\text{As}$ and p -type $\text{Li}_{0.95}(\text{Zn}_{0.95}, \text{Mn}_{0.05})\text{As}$ band structures. The similarity of the two curves shows that the position of the Fermi energy plays the dominant role in magnetic interactions while disorder effects associated with nonstoichiometric Li-(Zn,Mn) configurations are less important. Note that the two rigid-band curves border numerical data (not shown in the figure) obtained without imposing the rigid-band approximation. For comparison we plot in Fig. 3(a) E_{rev} obtained from the $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$ *ab initio* band structure (see also Ref. [20]). As expected the two compounds show very similar magnetic behavior.

The calculated positive values of E_{rev} at large hole concentrations correspond to ferromagnetic Mn-Mn coupling, consistent with experimentally observed ferromagnetic ground states in highly doped p -type (Ga,Mn)As. (At low hole concentrations E_{rev} changes sign and ferromagnetism becomes unstable due to the dominant role of short-range antiferromagnetic Mn-Mn superexchange [2].) The comparable strength of ferromagnetic Mn-Mn coupling for n -type and p -type doping at high carrier concentrations suggests that exchange interactions between Mn d states and conduction band states in zinc blende semiconductors can be strong and that Li(Zn,Mn)As with properly adjusted

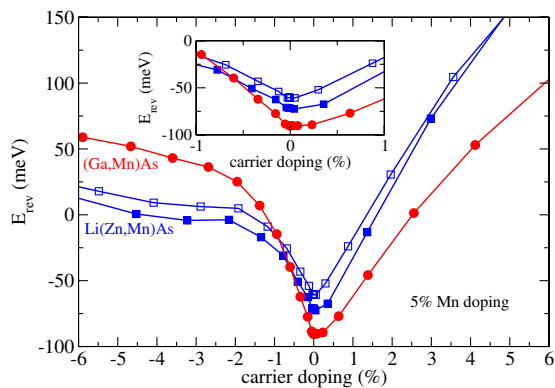


FIG. 3 (color online). Energy cost of flipping one Mn moment with all other Mn moments aligned. Open and closed squares were obtained from n -type $\text{Li}_{0.95}(\text{Zn}_{0.95}, \text{Mn}_{0.05})\text{As}$ and p -type $\text{Li}_{0.95}(\text{Zn}_{0.95}, \text{Mn}_{0.05})\text{As}$ *ab initio* band structures, respectively (see text for details). Circles represent calculations for $\text{Ga}_{0.95}\text{Mn}_{0.05}\text{As}$.

stoichiometry is a high Curie temperature n -type ferromagnetic semiconductor.

We now discuss the physical origin of the high-temperature electron-mediated ferromagnetism. In zinc blende semiconductors doped with Mn d^5 impurities, the local moments can have either a direct exchange interaction with band electrons on the same site and/or an interaction due to sp - d hybridization between the Mn local moment and band electrons on neighboring sites [21,22]. The latter interaction is typically much stronger and high-temperature ferromagnetism is expected to occur only when the hybridization coupling mechanism is present. In GaAs, the valence-band edge at the Γ point has a p -orbital character with a larger contribution from As [23]. Since the density of states at the valence-band edge is large, the occupied states for typical hole densities in ferromagnetic (Ga,Mn)As are still close to the Γ point and have similar atomic orbital composition. The p - d hybridization is allowed by symmetry within the whole Fermi sea which, together with the large magnetic susceptibility of heavy mass holes, explains the experimentally observed robust ferromagnetism in p -type (Ga,Mn)As.

The bottom of the conduction band of GaAs has an s -orbital character with a larger contribution from Ga. The smaller admixture of orbitals from the nearest neighbor As atoms to Mn_{Ga} , the vanishing s - d hybridization at the Γ point due to symmetry, and the small magnetic susceptibility of low effective mass electrons near the bottom of the conduction band all suggest that ferromag-

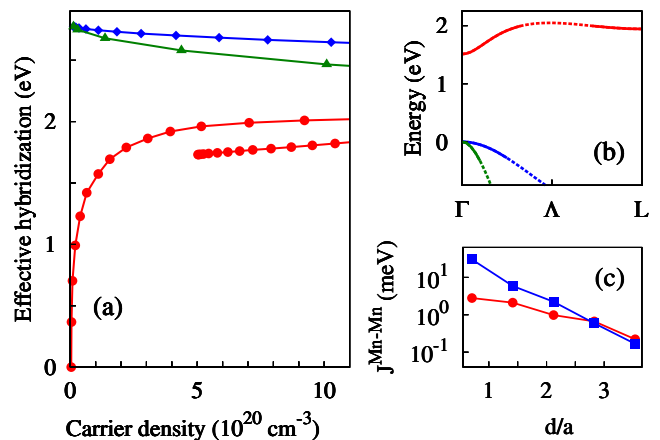


FIG. 4 (color online). (a) Model calculations of Mn_{Ga} d -orbital hybridization potentials with GaAs sp orbitals at the Fermi energy in the valence band (blue diamonds and green triangles) and conduction band (red circles) as a function of hole density and electron density, respectively. (b) Model band structure of the GaAs host illustrating the filled conduction band states (red full line) and empty valence-band states (black and blue lines) for electron or hole density of 10^{21} cm^{-3} [largest carrier density considered in panel (a)]. (c) *Ab initio* Mn-Mn exchange interactions as a function of Mn interatomic distance evaluated along the [110] crystal direction.

netism is unfavorable in n -type systems. The inset of Fig. 3 indeed shows a weaker tendency towards ferromagnetism in n -type materials, however, only at relatively low dopings.

To explain the seemingly unexpected robust ferromagnetism at larger electron concentrations we present, in Figs. 4(a) and 4(b), tight-binding model calculations of energy dependent sp - d hybridization in the conduction band and compare with the more familiar valence-band case. When moving off the Γ point, the hybridization rapidly sets in partly due to the s - d hybridization allowed by symmetry at nonzero wave vectors and partly due to the admixture of As and Ga p orbitals which increases with increasing wave vector. The strength of the sp - d hybridization in highly doped n -type systems, which includes all five d orbitals, becomes comparable to that of p -type materials as the Fermi energy leaves the bottom of the conduction band, and approaches the L point. The same picture which we have discussed for the familiar GaAs host doped with Mn, applies to Li(Zn,Mn)As whose material properties, as shown above, are much more favorable for achieving large n -type doping.

Within the mean-field theory, the ferromagnetic Curie temperature T_c can be estimated as $T_c \approx E_{\text{rev}}/6k_B$. The mean-field approximation should be reliable when the carrier mediated Mn-Mn coupling is sufficiently long range but tends to overestimate T_c when the carriers become more localized and magnetic interactions short-ranged [24–26]. In Fig. 4(c) we plot the spatially dependent interatomic exchange energies obtained by mapping the LDA + U /CPA total energies on the Heisenberg Hamiltonian [12]. As seen in the figure, the n -type Li(Zn,Mn)As shows very similar magnetic interaction characteristics to the p -type (Ga,Mn)As with corresponding doping densities. In both systems the leading exchange interactions are ferromagnetic and the interaction range safely exceeds the average Mn-Mn moment distance. Consistent with the theory expectations, experimental high quality (Ga,Mn)As materials show mean-field-like magnetization curves and Curie temperatures proportional to the density of Mn_{Ga} [17]. Maximum Mn_{Ga} doping achieved so far is approximately 6% and the corresponding record T_c is 173 K [17]. Calculations shown in Figs. 3 and 4 suggest comparable Curie temperatures for the n -type Li(Zn,Mn)As counterparts. Since we found no doping limit for Mn_{Zn} and straightforward means of high electron doping, Li(Zn,Mn)As might lead not only to the realization of a high Curie temperature diluted magnetic semiconductor with electron conduction but also might allow for larger magnetic moment density and therefore larger maximum T_c than (Ga,Mn)As.

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