

**Structural, electronic, and magnetic properties of  $\alpha$ - and  $\beta$ -MnAs: LDA and GGA investigations**

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Zinc-blende ( $\alpha$ -) and NiAs-type ( $\beta$ -) MnAs are investigated with a combined first-principles linearized augmented plane wave and DMol<sup>3</sup> study within both the local density approximation (LDA) and the generalized gradient approximation (GGA). First-principles calculations within the GGA predict the lattice volume for  $\beta$ -MnAs much better than LDA (which underestimates it by 15%) compared with experiment. The LDA calculated equilibrium lattice volume of  $\alpha$ -MnAs is 10% smaller than that of GaAs, which is in contradiction to the well-accepted fact that the lattice volume of Ga<sub>1-x</sub>Mn<sub>x</sub>As increases with  $x$ . In contrast, the GGA predicts a reasonable lattice volume for  $\alpha$ -MnAs. The ferromagnetic  $\alpha$ -MnAs is shown to be a metal at  $a = 5.7$  Å, and to undergo a transition to a half-metallic phase when it expands to  $a > 5.8$  Å due to the decreased bandwidth. Further, the calculated cohesive energy of  $\beta$ -MnAs is nearly 0.87 eV greater than that of  $\alpha$ -MnAs, which provides theoretical support for the instability of  $\alpha$ -MnAs.

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The recent discovery of carrier-induced ferromagnetism (FM) in Ga<sub>1-x</sub>Mn<sub>x</sub>As has generated intense interest,<sup>1-3</sup> mostly because of the possibility of developing devices combining information processing and storage functionalities in one material. The nature of FM in magnetic semiconductors is not clear, and is a major focus of recent experimental and theoretical works.<sup>1-5</sup> The simplest chemical structure of the magnetic semiconductor, Mn<sub>x</sub>Ga<sub>1-x</sub>As, is 100% Mn doped, i.e., zinc-blende MnAs. Although bulk zinc-blende MnAs is unstable, theoretical studies of this system, as well as of stable NiAs-type MnAs, may provide help in understanding the nature of FM in magnetic semiconductors.

In this Brief Report, we present results of a combined DMol<sup>3</sup> (i.e., density-functional for molecules and three-dimensional periodic solids<sup>6</sup>) and first-principles full-potential linearized-augmented-plane-wave method (FLAPW)<sup>7</sup> investigation of the structural, electronic and magnetic properties of  $\alpha$ - and  $\beta$ -MnAs, employing both the generalized gradient approximation (GGA) and the local-density approximation (LDA) within density-functional theory (DFT).

DMol<sup>3</sup> uses fast convergent three-dimensional numerical integrations to calculate the matrix elements occurring in the Ritz variational method. The basic description of the DMol method for molecules can be found in Ref. 8. The localized numerical linear combinations of atomic orbitals used as basis sets are designed to give maximum accuracy for a given basis set size. The atomic response to the molecular or solid environment can be handled robustly to an excellent approximation by a relatively small number of additional numerical functions.<sup>8</sup> The step from finite molecules and clusters to solids is done, as usual, by idealizing the solid with perfect translation symmetry of a unit cell.<sup>6</sup> The molecular sum over orbitals generalizes into an integration over the first Brillouin zone. DMol<sup>3</sup> has been successfully applied to band-structure calculations of insulating and metallic solids<sup>6</sup> and the complex structure of the BaTiO<sub>3</sub> grain boundary.<sup>9</sup>

In this work, a double set of numerical valence functions with a local basis cutoff  $R_c$  of 9.0 a.u. is employed. When a standard extended basis set and an  $R_c$  of 11.0 a.u. are tested for  $\alpha$ -MnAs, no remarkable changes for the lattice constant appear. Both the LDA functional, with formulas of Perdew and Wang<sup>10</sup> (PWC), and the GGA functional, with formulas of Perdew, Burke, and Ernzerhof<sup>11</sup> (PBE), are used in this work to illustrate the dependence of our theoretical predictions on functional treatments. In addition, a DMol<sup>3</sup> calculation with an effective core potential (ECP) of the Stuttgart-Dresden<sup>12,13</sup> group is also carried out, in order to assess the reliability of pseudopotentials on MnAs-type systems.

Calculations are also carried out with the highly precise FLAPW method, since DMol<sup>3</sup> is a newly developed method and a novice in spin-polarized solid systems. The FLAPW method is one of the most accurate *ab initio* methods, in which there is no artificial shape approximation for the wave functions, charge density, and potential. For all Ga, Mn, and As atoms, the core states are treated fully relativistically and the valence states are treated semirelativistically (i.e., without spin-orbit coupling). Muffin-tin (MT) radii for Ga and Mn are chosen as 2.40 a.u., and 2.00 a.u. is used for As. An energy cutoff of 12.25 Ry was employed for the augmented-plane-wave basis to describe the wave functions in the interstitial region, and a 49-Ry cutoff was used for the star functions depicting the charge density and potential. Within the MT spheres, lattice harmonics with angular momentum  $l \leq 8$  were adopted. In these FLAPW calculations, the LDA Hedin-Lundqvist formula<sup>14</sup> and the GGA functional with the same formulas as used in DMol<sup>3</sup> [PBE (Ref. 11)] are employed. The LDA formula used in the DMol<sup>3</sup> calculation is not the same as in FLAPW, because the PWC method is conventionally employed for DMol<sup>3</sup>/LDA calculations. We tried a DMol<sup>3</sup> calculation with the Hedin-Lundqvist formula for  $\alpha$ -MnAs, and no appreciable difference from the PWC result was found for the lattice constant (5.44 vs 5.43 Å).

TABLE I. Comparison of lattice constants (in Å), for  $\alpha$ -,  $\beta$ -MnAs, and GaAs within different exchange-correlation functional treatments, as well as with all-electron and pseudopotential bases. (Detailed descriptions of the functionals and pseudopotentials are given in the text.) For  $\beta$ -MnAs, the  $c/a$  ratio is fixed as the experimental value, 1.54, during the optimization. As a test,  $c/a$  was optimized with DMol<sup>3</sup>/GGA, which gives 1.53, i.e., very close to the experimental value.

Methods	Experiment	LDA				GGA		
		FLAPW	DMol <sup>3</sup>		SPECTER <sup>a</sup>	FLAPW	DMol <sup>3</sup>	
pseudopotential	–	–	–	ECP	HSC/optimized	–	–	ECP
GaAs	5.65 <sup>b</sup>	5.64	5.64	5.68		5.77	5.76	5.79
$\alpha$ -MnAs	–	5.45	5.43	5.61	5.6–5.7	5.68	5.70	5.87
$\beta$ -MnAs	3.7 <sup>c</sup>	3.48	3.50	3.59	3.60	3.66	3.67	3.75

<sup>a</sup>Reference 19.

<sup>b</sup>Reference 22.

<sup>c</sup>Reference 23.

Lattice constants for FM  $\alpha$ - and  $\beta$ -MnAs were investigated extensively, including a treatment of different functionals and pseudopotentials, and the results are listed in Table I. Some previous experimental and theoretical values for MnAs, as well as for GaAs, are also listed. Two conclusions can be obtained from Table I.

First, the LDA is qualitatively incorrect, and nonlocal corrections are necessary for MnAs. For  $\beta$ -MnAs, the LDA underestimates the lattice constant by about 5% in comparison with experiment, while the GGA gives a much better prediction (within 1% of experiment). It is well known that the lattice constant of  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$  obeys Vegard's law very well experimentally,<sup>1</sup> when  $x$  is smaller than 7%. Therefore, it is believed that the lattice constant of MnAs with the same structure, i.e.,  $\alpha$ -MnAs, is at least greater than that of GaAs. However, the theoretical LDA result gives  $\sim 5.45$  Å for  $\alpha$ -MnAs, which is much smaller than the lattice constant of GaAs: 5.65 Å. Thus it is strongly believed that the LDA is also qualitatively incorrect for  $\alpha$ -MnAs as for  $\beta$ -MnAs. It has been reported that the GGA gives better bond lengths of Fe (Ref. 16) and some  $3d$  transition-metal compounds, such as Mn-P in  $\text{MnGeP}_2$  (Ref. 17) and Co-S in  $\text{CoS}_2$ ,<sup>18</sup> although most GGA calculations overestimate the equilibrium volume. Both FLAPW and DMol<sup>3</sup> GGA calculations give  $\sim 5.7$  Å for  $\alpha$ -MnAs, which is clearly more correct than the LDA results.<sup>15</sup>

Second, it appears that all-electron calculations are required for MnAs systems. In Table I, it is clear that the all-electron FLAPW and DMol<sup>3</sup> calculations are in very good agreement with each other for  $\alpha$ - and  $\beta$ -MnAs and GaAs—which are the most reliable first-principles predictions for these lattice constants. The DMol<sup>3</sup>/ECP calculation is consistent with the all-electron calculations for GaAs, but not for MnAs. Actually, ECP overestimates the lattice constant for MnAs, which brings the LDA results with a pseudopotential close to the all-electron GGA results. The results of the SPECTER (a DFT pseudopotential plane-wave method) calculation,<sup>19</sup> with an optimized pseudopotential<sup>20</sup> for Mn and standard Hamann-Schülter-Chiang (HSC) pseudopotential<sup>21</sup> for As, gives 5.6–5.7 Å for  $\alpha$ -MnAs and

3.60 Å for  $\beta$ -MnAs; these poor results are very close to our DMol<sup>3</sup>/ECP results. Obviously, the same problem occurs with the HSC pseudopotential when dealing with MnAs, and hence indicates that both ECP and HSC pseudopotentials show their poor portability for MnAs, although they are fine for GaAs.

In addition, the cohesive energy of  $\alpha$ -MnAs, 6.41 eV, from the DMol<sup>3</sup>/GGA calculation at the theoretical equilibrium lattice constant, is around 0.87 eV less than that of  $\beta$ -MnAs. This provides strong theoretical support that  $\beta$ -MnAs is much more stable than  $\alpha$ -MnAs.

The energy differences (cf. Table II) between FM and simple antiferromagnetic (AFM) coupling MnAs systems are calculated with DMol<sup>3</sup> within the GGA based on their corresponding theoretical equilibrium structures. The AFM configuration is described as a superlattice of period  $p$  and layer orientation  $\mathbf{G}$  in Table II. Here  $\beta$ -MnAs, which is a FM material at room temperature, is seen to lie 51 meV per Mn atom lower in energy than the calculated AFM coupling along the [001] direction. The calculated energy difference between FM and simple AFM coupling (along the [110] directly) for  $\alpha$ -MnAs is very close to that of  $\beta$ -MnAs.

The total spin moments from DMol<sup>3</sup>/GGA are  $3.93\mu_B$  and  $2.86\mu_B$  per Mn atom for  $\alpha$ - and  $\beta$ -MnAs, respectively, and are in good agreement with the FLAPW/GGA results,  $3.84\mu_B$ , Refs. 22 and 23 in Table I, and  $2.98\mu_B$ , respectively. The experimental value for  $\beta$ -MnAs is  $\sim 3.4\mu_B$ , and so is greater than the calculated  $T=0$  K values which do not

TABLE II. The DMol<sup>3</sup>/GGA calculated energy difference between FM and AFM MnAs,  $\Delta E = E_{AFM} - E_{FM}$ . The spin superlattice with an AFM configuration is described as a superlattice of period  $p$  and layer orientation  $\mathbf{G}$ . The theoretical equilibrium constants 5.70 Å for  $\alpha$ -MnAs and 3.66 Å, with  $c/a=1.54$  for  $\beta$ -MnAs, are used in the calculations.

	$p$	$\mathbf{G}$	$\Delta E$ (meV/Mn)
$\alpha$ -MnAs	1	[110]	53
$\beta$ -MnAs	1	[001]	51

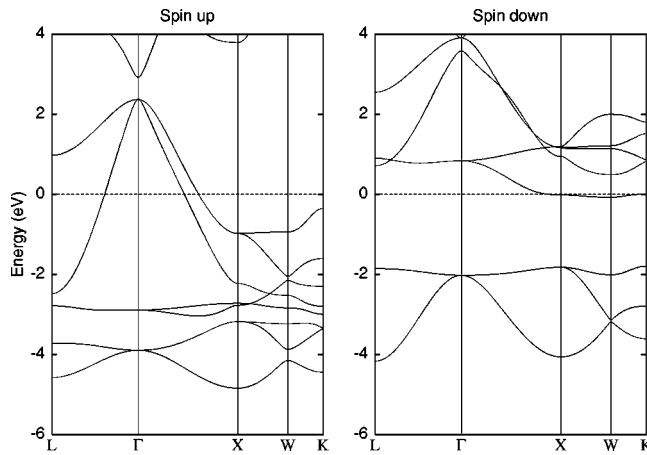


FIG. 1. Band structure of  $\alpha$ -MnAs from the DMol<sup>3</sup>/GGA calculation at a lattice constant of 5.70 Å. The Fermi level is set to zero.

include spin-orbit coupling. The spin moment for  $\alpha$ -MnAs is close to the expected value,  $4.0\mu_B$ , since each Mn provides three electrons to complete the bonds with nearest As atoms. In the LDA case, the calculated moments are only around  $2.8\mu_B$  and  $2.1\mu_B$  for the optimized  $\alpha$ - and  $\beta$ -MnAs, respectively, and so are much smaller than the GGA results or experiment.<sup>24</sup> The DMol<sup>3</sup> calculated band structure in Fig. 1, indicates that  $\alpha$ -MnAs just misses being half-metallic at  $a = 5.70$  Å. Our further calculations show that it will experience a phase transition to a half-metallic state when the lattice constant is stretched to  $>5.8$  Å. This may be ascribed to the bandwidth decreasing from the increasing atomic distance. For instance, the width of the lowest spin-down conduction band is reduced by 100 meV when  $a$  expands from 5.70 to 5.80 Å. The reduced bandwidth enlarges the band gap in the spin-down band structure, and causes a transition to a half-metallic state.

The density of states in Fig. 2 indicates that the Mn 3d bands are much more localized in energy for  $\alpha$ -MnAs than for  $\beta$ -MnAs, which results from the different crystal symmetry. The exchange splitting (the average energy difference between spin-down and up bands) of Mn 3d is 3.33 eV for  $\alpha$ -MnAs and 2.56 eV for  $\beta$ -MnAs. The large exchange splitting energy keeps a MnAs structure in the high-spin-state ordering, as in  $\text{Ga}_{1-x}\text{Mn}_x\text{As}$ .<sup>5</sup> The broader bands and smaller exchange splitting energy of Mn 3d in  $\beta$ -MnAs causes its magnetic moment to be smaller than that of  $\alpha$ -MnAs. The band structure and density-of-states plots obtained from DMol<sup>3</sup> calculations are in excellent agreement with the FLAPW results.

In summary, we calculated the lattice constants of  $\alpha$ - and  $\beta$ -MnAs in a combined FLAPW and DMol<sup>3</sup> study within

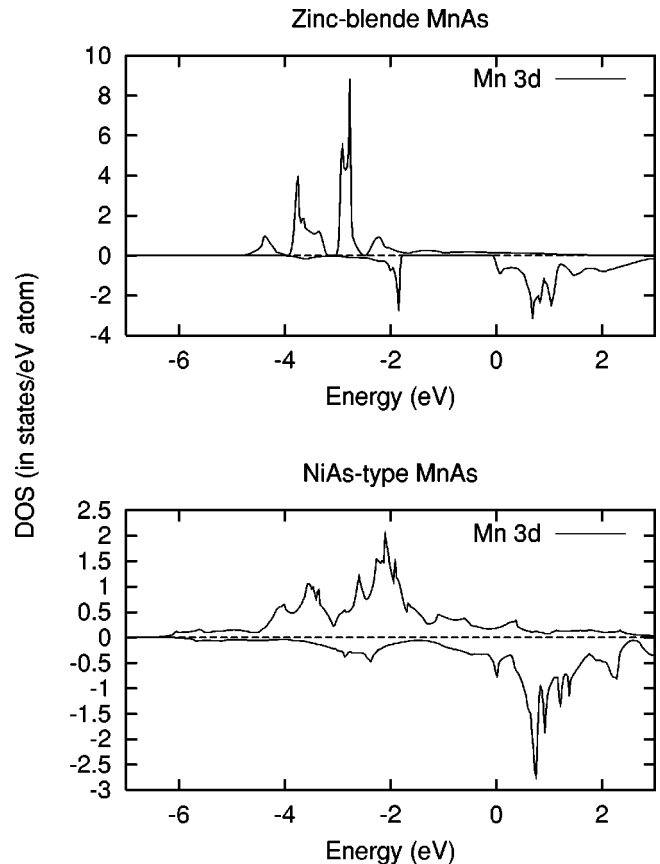


FIG. 2. Mn 3d density of states (DOS) in  $\alpha$ - and  $\beta$ -MnAs from DMol<sup>3</sup>/GGA calculations at their theoretical equilibrium lattice constants, with spin-up positive and spin-down negative. The Fermi level is set to zero.

both the LDA and GGA. We found that the LDA underestimates the lattice constants for MnAs systems by around 5%, and that the GGA appears to be necessary for better results. Since poor portability shows up for some pseudopotentials in MnAs, all-electron calculations seem to be required. Furthermore,  $\alpha$ -MnAs is not half-metallic at the theoretical equilibrium structure (5.70 Å), but it will be if the lattice constant is stretched to become greater than 5.80 Å by, for example, epitaxial growth on a larger lattice constant substrate. Hence it would possibly be useful as a source of spin-polarized electrons in spintronic devices made with magnetic semiconductors.

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<sup>1</sup>H. Ohno, Science **281**, 951 (1998).

<sup>2</sup>Y. Ohno, D.K. Young, B. Beschoten, F. Matsukura, H. Ohno, and D.D. Awschalom, Nature (London) **402**, 790 (1999).

<sup>3</sup>T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).

<sup>4</sup>Jürgen König, Hsiu-Hau Lin, and Allan H. MacDonald, Phys.

Rev. Lett. **84**, 5628 (2000).

<sup>5</sup>Yu-Jun Zhao, W.T. Geng, K.T. Park, and A.J. Freeman, Phys. Rev. B **64**, 035207 (2001).

<sup>6</sup>B. Delley, J. Chem. Phys. **113**, 7756 (2000).

<sup>7</sup>E. Wimmer, H. Krakauer, M. Weinert, and A.J. Freeman, Phys. Rev. B **24**, 864 (1981), and references therein; H.J.F. Jansen and

- A.J. Freeman, Phys. Rev. **30**, 561 (1984).
- <sup>8</sup>B. Delley, J. Chem. Phys. **92**, 508 (1990).
- <sup>9</sup>W.T. Geng, Yu-Jun Zhao, A.J. Freeman, and B. Delley, Phys. Rev. B **63**, 060101 (2001).
- <sup>10</sup>J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).
- <sup>11</sup>J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- <sup>12</sup>M. Dolg, U. Wedig, H. Stoll, and H. Preuss, J. Chem. Phys. **86**, 866 (1987).
- <sup>13</sup>A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss, Mol. Phys. **80**, 1431 (1993).
- <sup>14</sup>L. Hedin and B.I. Lundqvist, J. Phys. C **4**, 2064 (1971).
- <sup>15</sup>It is necessary to point out that M. Shirai, T. Ogawa, I. Kitagawa, and N. Suzuki, J. Magn. Magn. Mater. **177-181**, 1383 (1998), obtained 5.9 Å for  $\alpha$ -MnAs, i.e., much greater than our results. Noting that the muffin-tin spheres are not fixed during their calculation, we realize that they might overestimate the lattice constant by this error.
- <sup>16</sup>T. Asada and K. Terakura, Phys. Rev. B **46**, 13 599 (1992).
- <sup>17</sup>Yu-Jun Zhao, W.T. Geng, A.J. Freeman, and T. Oguchi, Phys. Rev. B **63**, 201202 (2001).
- <sup>18</sup>T. Shishido, A.J. Freeman, and R. Asahi, Phys. Rev. B **64**, 180401 (2001).
- <sup>19</sup>S. Sanvito and N.A. Hill, Phys. Rev. B **62**, 15 553 (2000).
- <sup>20</sup>A.M. Rappe, K.M. Rabe, E. Kaxiras, and J.D. Ioannopolous, Phys. Rev. B **41**, 1227 (1990).
- <sup>21</sup>D.R. Hamann, M. Schülter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).
- <sup>22</sup>J. Singh, *Physics of Semiconductors and Their Heterostructures* (McGraw-Hill, New York, 1993).
- <sup>23</sup>F. Schippan, M. Kästner, L. Däweritz, and K.H. Ploog, Appl. Phys. Lett. **76**, 834 (2000).
- <sup>24</sup>Interestingly, the result of Ref. 19, with an incorrect LDA lattice constant (which comes out to be close to our GGA value), yields moments that are close to our GGA values.