

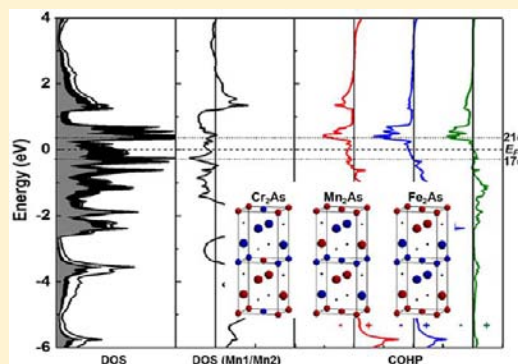
Magnetic Ordering in Tetragonal 3d Metal Arsenides M_2As ($M = Cr, Mn, Fe$): An Ab Initio Investigation

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Supporting Information

ABSTRACT: The electronic and magnetic structures of the tetragonal Cu_2Sb -type 3d metal arsenides (M_2As , $M = Cr, Mn, Fe$) were examined using density functional theory to identify chemical influences on their respective patterns of magnetic order. Each compound adopts a different antiferromagnetic (AFM) ordering of local moments associated with the 3d metal sites, but every one involves a doubled crystallographic c -axis. These AFM ordering patterns are rationalized by the results of VASP calculations on several magnetically ordered models using $a \times a \times 2c$ supercell. Effective exchange parameters obtained from SPRKKR calculations indicate that both direct and indirect exchange couplings play essential roles in understanding the different magnetic orderings observed. The nature of nearest-neighbor direct exchange couplings, that is, either ferromagnetic (FM) or AFM, were predicted by analysis of the corresponding crystal orbital Hamilton population (COHP) curves obtained by TB-LMTO calculations. Interestingly, the magnetic structures of Fe_2As and Mn_2As show tetragonal symmetry, but a magnetostriuctive tetragonal-to-orthorhombic distortion could occur in Cr_2As through AFM Cr1–Cr2 coupling between symmetry inequivalent Cr atoms along the a -axis, but FM coupling along the b -axis. A LSDA+U approach is required to achieve magnetic moment values for Mn_2As in better agreement with experimental values, although computations always predict the moment at the M1 site to be lower than that at the M2 site. Finally, a rigid-band model applied to the calculated DOS curve of Mn_2As correctly assesses the magnetic ordering patterns in Cr_2As and Fe_2As .



1. INTRODUCTION

The discovery of superconductivity in tetragonal iron-arsenide based compounds has resulted in a multitude of research to investigate materials with similar compositions or structures, for example, $[LaO_{1-x}F_x][FeAs]$,¹ $Ba_{0.6}K_{0.4}[Fe_2As_2]$,² $LiFeAs$,^{3,4} and $NaFeAs$.^{5,6} One class of compounds that has been overlooked thus far are the 3d metal arsenides with the general composition M_2As ($M = Cr, Mn, Fe$). These compounds crystallize in the tetragonal Cu_2Sb -type structure (space group $P4/nmm$),⁷ which is illustrated in Figure 1. The transition metals in these compounds occupy two distinct crystallographic sites, labeled as M1 (orange) and M2 (purple). Each M1 site is coordinated by a distorted tetrahedron of 4 As atoms and surrounded by a square planar arrangement of M1 sites to produce a planar square net of M1 atoms. This structural fragment, which has the unit cell formula $[M_1As_2]$ corresponds to the iron-arsenide layers found in the superconductors. On the other hand, the M2 site is coordinated by a square pyramid of 5 As atoms and caps planar squares formed by M1 sites. The M2 sites together with the As atoms form $[M_2As_2]$ bilayers that resemble distorted bilayers extracted from a rocksalt structure. The $[M_1As_2]$ layer and $[M_2As_2]$ bilayers stack alternately along the c -axis, sharing As atoms, which leads to the formulation $[M_1As_{2/2}][M_2As_{2/2}] = (M_1)_2(M_2)_2As_2$ per crystallographic unit cell. Now, among

the iron-arsenide superconductors, antiferromagnetic (AFM) order is a competing ground state to superconductivity.⁶ Since all the binary 3d M_2As ($M = Cr, Mn, Fe$) compounds adopt antiferromagnetic ground states,^{7–10} and there have been no reports of superconductivity in them, studies of the factors influencing the magnetic order among various 3d metal arsenides could help to elucidate mechanisms of superconductivity in iron-arsenide superconductors.

According to Yuzuri et al.^{7,8} and Katsuraki et al.,⁹ all of the 3d metal arsenides M_2As ($M = Cr, Mn, Fe$) can be prepared as bulk powders (in limited cases, as single crystals) in relatively high yields. Each compound undergoes an AFM transition with Néel temperatures of 393, 573, and 353 K, respectively, for Cr_2As ,⁷ Mn_2As ,⁸ and Fe_2As .^{9,10} Additionally, neutron diffraction^{9–12} was used to identify the complex magnetic structure of each compound along with the values of the local magnetic moments. The room temperature diffraction studies show that the unit cell volumes increase then decrease along the sequence Cr_2As, Mn_2As, Fe_2As , while the c/a ratio decreases monotonically along the same sequence. Each 3d metal compound adopts a different AFM ground state involving a doubled crystallographic c -axis with the easy direction of each moment

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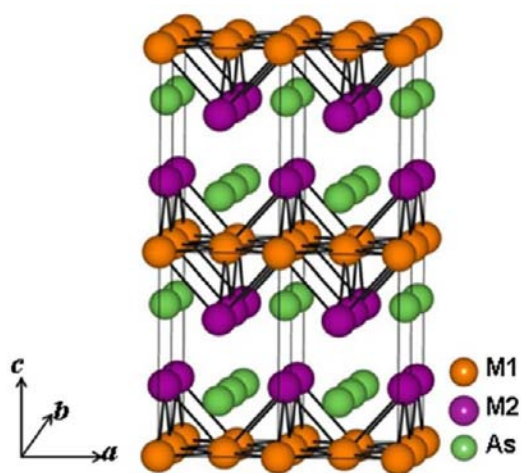


Figure 1. Crystal structure of tetragonal M_2As ($M = Cr, Mn, Fe$) viewed along the b -axis. Orange, purple, and green spheres, respectively, represent M1, M2, and As atoms. Lines are drawn to emphasize the nearest neighbor M1-M1 and M1-M2 contacts.

lying in the ab -plane. These magnetic structures and local magnetic moment values are summarized in Figure 2.

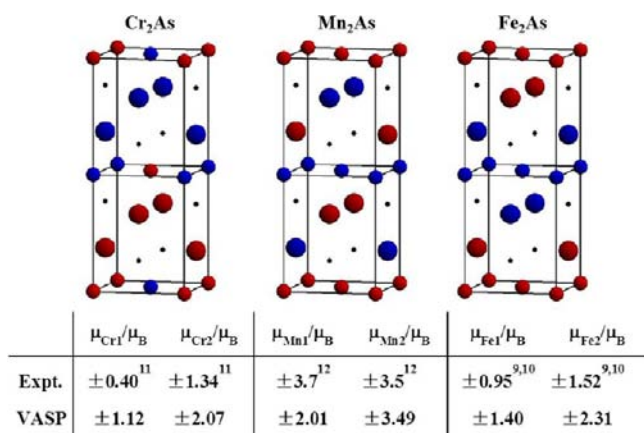


Figure 2. AFM ground state magnetic structures and the values of the local magnetic moments of M_2As ($M = Cr, Mn, Fe$). Small spheres, large spheres, and black dots represent, respectively, M1, M2, and As atoms. Red and blue colors indicate oppositely oriented magnetic moments.

In Cr_2As , which was studied by powder and single crystal neutron diffraction,¹¹ adjacent Cr1–Cr1 atoms within the square net are AFM coupled. Among the four nearest neighbor Cr1–Cr2 contacts, two along the a -axis are AFM coupled whereas the other two along the b -axis are coupled ferromagnetically. Thus, the magnetic ordering destroys the crystallographic tetragonal symmetry. Near-neighbor Cr2–Cr2 contacts are ferromagnetic (FM), whereas next near-neighbor Cr2–Cr2 interactions, which occur across the square nets of Cr1 atoms, are AFM. Mn_2As has been characterized by powder neutron diffraction,¹² which indicated FM coupling for nearest neighbor Mn1–Mn1 contacts and AFM Mn1–Mn2 interactions. In Fe_2As , powder and single crystal neutron diffraction^{9,10} results gave FM Fe1–Fe1 and Fe1–Fe2 nearest neighbor interactions, which creates FM slabs that are AFM coupled by near neighbor Fe2–Fe2 interactions along the c -axis.

A few electronic structure calculations^{13–16} have attempted to identify as well as explain the magnetic ordering in the M_2As ($M = Cr, Mn, Fe$) series. For example, Rahman¹⁵ argued that the stability of the ground state magnetic structure in Mn_2As , in particular, could be attributed to significant nearest neighbor Mn1–Mn2 AFM interactions. Motizuki et al.¹⁶ examined the entire series using a Hubbard-type model and reported that the bonding nature of the electronic bands near the Fermi level as well as the presence of a nesting effect of the Fermi surface play the important roles to develop the different magnetic orderings in these Cu_2Sb -type compounds. However, none of these computational investigations comprehensively investigated various competing magnetic structures for each compound, nor did they analyze the electronic structure with respect to interatomic orbital and exchange interactions.

Clearly, these 3d metal arsenides contain numerous magnetic exchange pathways, which make identifying the preferred magnetic ordering and predicting any changes in magnetic behavior as a function of composition challenging. Herein, we report an analysis of the electronic structures of the 3d metal arsenides, M_2As ($M = Cr, Mn, Fe$), to identify the origin of the resulting magnetic structures and to provide insights into the influence of metal–metal orbital interactions on magnetic ordering. Total energy calculations are employed initially to identify the most electronically favorable magnetic structure as a function of composition. Additionally, pairwise effective exchange parameters are calculated to identify the coupling constants between the independent metal atoms in the series of 3d metal arsenides. Finally, electronic instabilities that could manifest long-range magnetic ordering are identified via metal–metal crystal orbital Hamilton population (COHP) curves.^{17–21} Electronic band structure plots are also provided to examine the potential electronic driving forces of the nearest neighbor M2-M2 exchange couplings in M_2As .

2. COMPUTATIONAL DETAILS

To investigate the magnetic ordering and the corresponding electronic structures of M_2As ($M = Cr, Mn, Fe$), a combination of computational methods was utilized to accomplish three goals. These are: (i) to evaluate the relative total energies of different magnetically ordered structures of each system; (ii) to evaluate the effective metal–metal exchange interactions in the ground state magnetic structures; and (iii) to calculate the electronic band structures and densities of states (DOS) of the ground state magnetic structures, as well as to analyze the interatomic orbital interactions using COHP analysis. For all calculations, local magnetic moments are determined by the difference between the numbers of up-spin and down-spin electrons associated with each site. Spin–orbit coupling was not included, so orientations of magnetic moment pseudovectors were not calculated.

(i). Total Energies of Magnetically Ordered M_2As Systems.

Twelve distinct magnetic structures were constructed using the lattice parameters and atomic positions for each phase as summarized by Pearson (Supporting Information, Table S1).²² The magnetic structures are differentiated by the specific nearest and next nearest neighbor M1–M1, M1–M2, and M2–M2 exchange interactions. Among these configurations of magnetic moments, 1 is ferromagnetic (F), 1 is ferrimagnetic (Fi), and 10 are antiferromagnetic (AF1–AF10). They are illustrated in Figure 3, and each is labeled by its magnetic space group. Three magnetic structures correspond to the crystallographic unit cell, namely, F, Fi, and AF5, whereas the remaining nine cases require a doubled c -axis. The total energies and electronic structures of these magnetic models were determined for each system using the projector augmented wave method (PAW) of Blöchl^{23,24} coded in the Vienna ab initio simulation package (VASP).²⁵ All VASP calculations employed the generalized gradient approximation (GGA) with exchange and correlation treated by Perdew–Burke–Erzerhoff

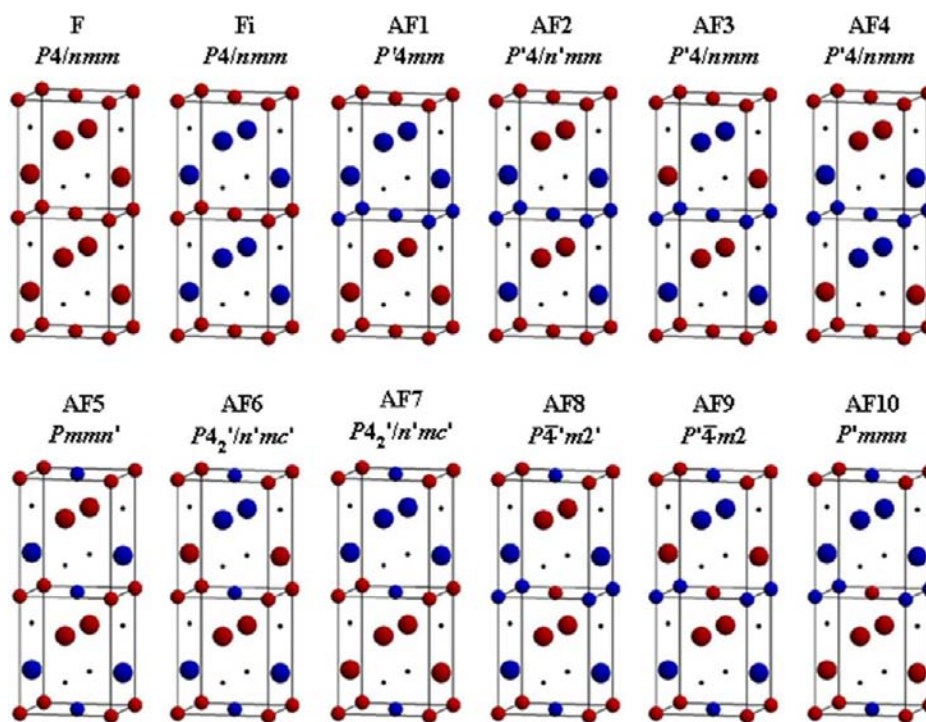


Figure 3. Twelve possible magnetic structures and their magnetic space groups constructed from tetragonal M_2As ($M = Cr, Mn, Fe$) unit cells doubled along the c -axis. Small spheres, large spheres, and black dots represent M1, M2, and As atoms, respectively. Oppositely oriented magnetic moments, which are determined by the relative numbers of up-spin and down-spin electrons, are indicated by red and blue colors. Models F and Fi have nonzero net magnetization; Models AF1–AF10 have zero net magnetization.

(PBE).²⁶ The cutoff energies for the plane wave calculations was set to 500 eV and a mesh of $9 \times 9 \times 3$ k -points were used for integrations involving the irreducible wedge of the tetragonal Brillouin zone.

(ii). Effective Metal–Metal Exchange Parameters in Low Energy Magnetic Structures of M_2As . The effective exchange interactions between adjacent metal atoms in the ground state magnetic structures were evaluated using the spin-polarized, relativistic Korringa–Kohn–Rostoker (SPRKKR) package.²⁷ The effective intersite exchange parameters, J_{ij} between sites i and j are obtained from the effective Heisenberg Hamiltonian,

$$H_{\text{eff}} = -\sum_{ij} J_{ij} \mathbf{e}_i \cdot \mathbf{e}_j \quad (1)$$

where \mathbf{e}_i and \mathbf{e}_j are unit vectors representing the relative orientation of local magnetic moments on sites i and j . SPRKKR employs a local spin-density functional approach and the KKR Greens function formalism proposed by Liechtenstein et al.²⁸ to calculate the J_{ij} values between magnetically active sites i and j . All calculations employed GGA–PBE²⁶ for the exchange and correlation corrections and 1000 k -points in the Brillouin zone.

(iii). Electronic Structures of M_2As Systems. Once the ground state magnetic structures were determined for M_2As ($M = Cr, Mn, Fe$) by VASP from among the 12 models in Figure 3, their electronic density of states (DOS) and interatomic crystal orbital Hamiltonian population (COHP) curves were calculated and analyzed using the Stuttgart version of the tight-binding, linear muffin-tin orbital (TB-LMTO) method with the atomic spheres approximation.^{29,30} Within TB-LMTO, exchange and correlation were treated using the von Barth–Hedin local density (LDA) and local spin-density approximation (LSDA).³¹ All relativistic effects except spin–orbit coupling were taken into account using a scalar relativistic approximation.³² The basis sets include 4s and 4p wave functions for As, 3d, 4s, 4p wave functions for Cr, Mn, and Fe, and 1s wave functions for an empty sphere (E) located at the Wyckoff site $2b$ ($0, 0, \frac{1}{2}$) of the crystallographic unit cell. The As 3d and E 2p and 3d orbitals were treated by the Löwdin downfolding technique.³³ The Wigner-Seitz radii of atomic spheres were 1.44–1.48 Å for As, 1.39 and 1.43 Å for Cr, 1.44 and 1.48 Å for

Mn, and 1.38 and 1.39 Å for Fe. Together with the empty sphere with radii 0.98–1.04 Å, the unit cell is filled with about 9% total overlap. Sets of $12 \times 12 \times 8$ and $12 \times 12 \times 4$ k -points in the irreducible wedge of the tetragonal Brillouin zone were used for integrations over crystallographic unit cells and cells doubled along the c -axis, respectively.

3. RESULTS AND DISCUSSION

The three tetragonal, metal arsenides, Cr_2As , Mn_2As , and Fe_2As , adopt three distinct magnetic structures according to refinements of powder or single crystal neutron diffraction studies. The computational results using VASP give magnificent agreement with the experimental magnetic structures: the corresponding ground states are AF10 for Cr_2As ; AF3 for Mn_2As ; and AF4 for Fe_2As (see Figure 3).^{9,10,12} On the other hand, the local magnetic moments, which are presented in Figure 2, are slightly overestimated for Cr_2As and Fe_2As , and underestimated specifically for the Mn1 site in Mn_2As . Nonetheless, in all cases, the calculated moments at the M2 sites are larger than those on the M1 sites, which agree qualitatively with the results for Cr_2As and Fe_2As .^{9–11} However, in Mn_2As , there is significant disagreement for the magnetic moment on Mn1 between calculated values ($\pm 2.01 \mu_B$) and experimental observations ($\pm 3.7 \mu_B$). But our calculated magnetic moment on the Mn1 site ($\pm 2.01 \mu_B$) is comparable with the value calculated by Yang et al. ($\pm 1.89 \mu_B$)¹⁴ and Rahman ($\pm 1.98 \mu_B$).¹⁵ Further details of the VASP results, namely, relative total energies and local magnetic moments on the metal sites, are summarized in Supporting Information, Table S2.

To gain further insights about the exchange interactions leading to the various types of AFM ground states in Cr_2As , Mn_2As , and Fe_2As , effective exchange parameters for nearest-

neighbor and next-nearest-neighbor metal–metal contacts were evaluated. These results are summarized in Table 1. The two

Table 1. Metal–metal Distances and Their Corresponding Effective Exchange Parameters (J_{ij}) Calculated for the Magnetic Ground States (VASP) of M_2As ($M = Cr, Mn, Fe$) Using the SPRKKR Program

	Cr_2As		Mn_2As		Fe_2As	
	distance (Å)	J (meV)	distance (Å)	J (meV)	distance (Å)	J (meV)
J_{M1-M1}	2.540	−14.1	2.665	−1.68	2.570	+25.4
J_{M1-M2}	2.734	−7.85 ^c	2.801	−14.5	2.684	+6.52
		−12.8 ^d				
J'_{M2-M2} ^a	3.373	+1.83	3.414	−19.6	3.278	−3.52
J''_{M2-M2} ^b	4.842	−6.02	4.926	−0.70	4.712	+8.52

^aNearest neighbor M2–M2 interaction. ^bM2–M2 exchange interaction linked through the M1 layer. ^c J_{M1-M2} along the a -axis. ^d J_{M1-M2} along the b -axis.

shortest contacts, M1–M1 and M1–M2, involve significant orbital overlap and may be classified primarily as *direct* exchange pathways. The two longer ones are nearest and next-nearest neighbor M2–M2 contacts, both of which may be identified primarily as *indirect* exchange pathways, although some *direct* exchange may participate between nearest neighbor sites. According to these results, the network of nearest neighbor metal–metal contacts (see Figure 1) in Fe_2As forms FM layers that are antiferromagnetically coupled via nearest neighbor Fe2–Fe2 interactions. On the other hand, the exchange parameters evaluated for Mn_2As and Cr_2As reveal some frustrated AFM interactions in each case, results that will be discussed in subsequent paragraphs.

Finally, for each case, the nonspin- (LDA) and spin-polarized (LSDA) electronic structures were calculated and analyzed using COHP curves for nearest neighbor orbital interactions and electronic band structures to provide some chemical insights into their different ground state magnetic structures. The presence of a peak in the DOS that also corresponds to M–M antibonding interactions is likely to drive an electronic reorganization, that is, spin-polarize and order ferromagnetically, as seen for body-centered cubic (bcc) α -Fe.^{18–21} Conversely, when the M–M interactions are nonbonding at the Fermi level (E_F), such as in bcc-Cr, the substance may exhibit AFM long-range ordering.^{20,21} In all three cases, the Fermi levels lie on peaks in the LDA DOS curves, that is, show large $N(E_F)$ values, which are listed in Table 2. Upon spin-polarization (LSDA), all $N(E_F)$ values decrease.

Fe_2As . The Fermi level in the LDA-based (nonspin-polarized) DOS curve lies clearly on a sharp peak (see Figure 4). These states also correspond to strongly antibonding Fe1–Fe1 and Fe1–Fe2 orbital interactions as seen in their COHP curves (Figure 4). Thus, to remove this electronic instability,

Table 2. DOS Values at Fermi Levels, $N(E_F)$,^a for M_2As as Determined by Non-Spin (LDA) and Spin-Polarized Treatment of Electronic States

	Cr_2As	Mn_2As	Fe_2As
LDA	3.81	5.21	12.7
LSDA	2.82	2.55	3.10

^aStates/eV per formula unit.

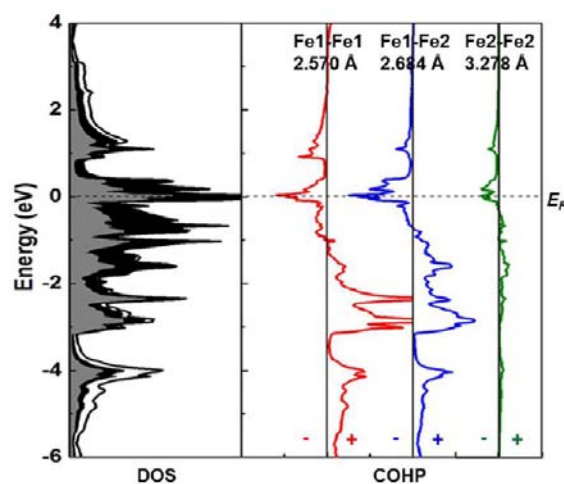


Figure 4. Nonspin-polarized DOS (gray, black, and white represent Fe1, Fe2, and As, partial DOS, respectively) and COHP curves for nearest neighbor Fe1–Fe1 (red), Fe1–Fe2 (blue), and Fe2–Fe2 (green) in Fe_2As . The Fermi level is indicated by the dashed line. + and – signs indicate bonding and antibonding interactions, respectively.

FM exchange coupling for both Fe1–Fe1 and Fe1–Fe2 nearest neighbor contacts is predicted,^{18–21} which agrees with the VASP, SPRKKR, and experimental results. This pattern of magnetic exchange creates FM slabs indicated by the shorter metal–metal contacts in Figure 1. The effective exchange parameters evaluated by the SPRKKR approach indicate a significantly larger Fe1–Fe1 interaction (+25.4 meV) than Fe1–Fe2 interaction (+6.52 meV). According to the results of VASP calculations, these slabs are preferred to be AFM coupled along the c -direction (AF4 in Figure 3) by 30.7 meV/f.u. (ca. 360 K/f.u.) over FM coupled slabs (F in Figure 3). The effective nearest neighbor Fe2–Fe2 exchange parameter is weakly AFM (−3.52 meV), which is also consistent with the total energy calculations. The corresponding Fe2–Fe2 COHP curve (shown also in Figure 4) also reflects weak interatomic orbital overlap because the distance is quite long (3.278 Å).

To examine any potential electronic driving forces for nearest neighbor AFM Fe2–Fe2 coupling, the LDA electronic band structure of Fe_2As was examined (see Supporting Information, Figure S2 for the complete band structures). Along the Brillouin zone boundary X – R , which is highlighted in Figure 5, the Fermi level intersects a narrow (~ 0.2 eV wide), doubly degenerate band that arises primarily from xz/yz at the Fe2 sites and $xy/xz/yz$ orbitals at the Fe1 sites. Its narrow dispersion arises from weak Fe2–Fe2 antibonding overlap at the R point but Fe2–As d–p(d) π -antibonding overlap at the X point. The participation of As valence orbitals in this band provides an AFM superexchange mechanism between nearest neighbor Fe2 sites because the xz and xy orbitals of Fe2 sites overlap substantially through the As p(d) orbitals. On doubling the unit cell along the c -axis, the original energy bands become “folded,”³⁴ and the Fermi level falls very nearly on a 4-fold degenerate band at the R' point, a result which resembles a band filling leading to a Peierls ($2k_F$) distortion for one-dimensional chain structures with a half-filled band.³⁵ Upon introducing spin polarization (LSDA), the symmetry controlled degeneracies at R' become broken by AFM coupling along the c -direction, and the bands split to create an energy gap around the Fermi level. The effective band splitting is similar to a spin-

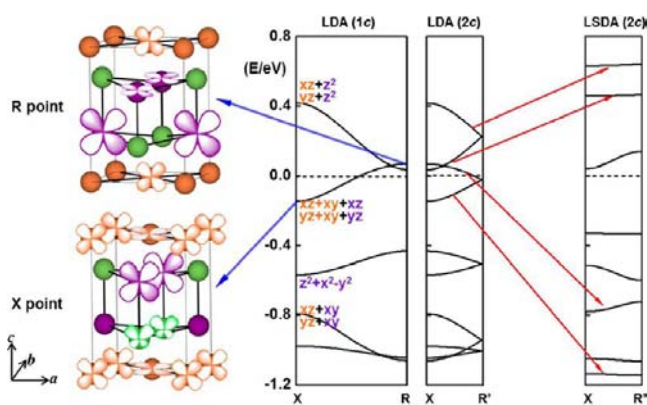


Figure 5. Electronic band structure plots near the Fermi level along X - R , $X = (\pi/a, 0, 0)$ and $R = (\pi/a, 0, \pi/c)$, on the Brillouin zone boundary of Fe_2As . (Left) Nonspin polarized (LDA) bands for the crystallographic unit cell (1c) (major d-orbital contributions from Fe1 (orange) and Fe2 (purple) are noted); (Middle) Nonspin polarized (LDA) bands for the unit cell doubled along the c -axis (2c), $R' = (\pi/a, 0, \pi/2c)$; (Right) Spin polarized (LSDA) majority/minority spin bands for the unit cell doubled along the c -axis (2c). Shifts in energy between LDA(2c) and LSDA(2c) bands are indicated by the red arrows. A depiction of the crystal orbitals at the X and R points of the band intersected by the Fermi level is included. The orbital at the X point is Fe2 xz (64%), Fe1 xz (16%), Fe1 xy (15%), and As $xz+p_x$ (1.4%). The orbital at the R point is Fe2 xz (46%), Fe1 xz (25%), and Fe2 xy (23%).

Peierls transition.³⁶ On the other hand, FM coupling along the c -direction, which is less preferred energetically, shifts the Fermi level away from the 4-fold degeneracy at the R' point, but does not create an energy gap surrounding E_F . Thus, Fe_2As can be viewed as FM slabs that are AFM coupled along the stacking (c) direction.

Mn_2As . Like Fe_2As , Mn_2As shows two low-energy magnetic structures that differ by their magnetic exchange interactions along the c -axis according to VASP calculations. The calculated ground magnetic state has a doubled c -axis because the nearest neighbor Mn2–Mn2 exchange interactions are AFM. Unlike Fe_2As , however, the Mn1–Mn2 interactions are decidedly AFM, whereas the Mn1–Mn1 coupling is FM. The low lying excited magnetic structure, which lies 19.3 meV/f.u. (ca. 220 K/f.u.) above the ground state, keeps the crystallographic unit cell by retaining FM Mn1–Mn1 and AFM Mn1–Mn2, but exhibiting FM nearest neighbor Mn2–Mn2 exchange. Thus, this higher energy configuration is ferrimagnetic (Fi), or uncompensated AFM.

The LDA-based DOS curve for Mn_2As , illustrated in Figure 6, shows that the Fermi level lies rather near a peak, which is characterized by weakly antibonding (indeed, nearly non-bonding) Mn1–Mn1 and Mn1–Mn2 orbital interactions in the corresponding COHP curves. Therefore, AFM Mn1–Mn1 and Mn1–Mn2 may be anticipated to alleviate the electronic instability associated with the large $N(E_F)$ value in Mn_2As . The calculated J_{ij} values listed in Table 1 confirm that AFM coupling is preferred for both Mn1–Mn1 and Mn1–Mn2 contacts. However, in the two low-energy magnetic structures, the Mn1–Mn1 interaction is FM, which must arise from frustration of competing Mn1–Mn1 and Mn1–Mn2 AFM exchange couplings. Since the Mn1–Mn2 exchange coupling (–14.5 meV) is about 9× larger than the Mn1–Mn1 coupling (–1.68 meV), and there are 4 Mn1–Mn2 contacts but 2 Mn1–Mn1 contacts per formula unit, the magnetic ground state of Mn_2As

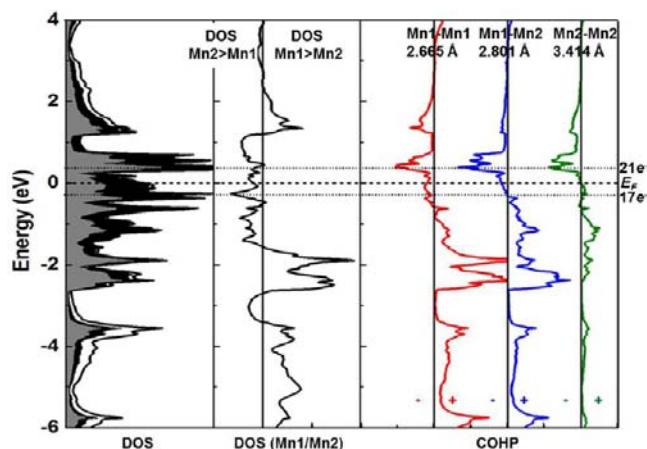


Figure 6. (Left) Nonspin-polarized DOS curves (gray, black, and white represent Mn1, Mn2, and As, partial DOS, respectively), (middle) Mn1/Mn2 DOS ratio, and (right) COHP curves for nearest neighbor Mn1–Mn1 (red), Mn1–Mn2 (blue), and Mn2–Mn2 (green) in Mn_2As . The Fermi level ($19e^-/\text{f.u.}$) is indicated by the dashed line; Fermi levels for $17e^-/\text{f.u.}$ (“ Cr_2As ”) and $21e^-/\text{f.u.}$ (“ Fe_2As ”) are indicated by the dotted lines. + and – signs indicate bonding and antibonding interactions, respectively.

will be dictated by the Mn1–Mn2 interactions. Hence, the magnetic moments of the Mn1 sites are FM coupled with each other.

To analyze the nearest neighbor Mn2–Mn2 exchange coupling, the LDA electronic band structure along special Brillouin zone boundaries parallel to c^* , that is, Γ -Z, X -R, and M -A, were examined (see Supporting Information, Figure 3S). The Fermi level intersects bands only along the Γ -Z line; there are energy gaps for the other two boundary lines. Thus, we focus on the Γ -Z direction in Figure 7. In the LDA band structure, the Fermi level intersects a broad (~ 0.8 eV wide),

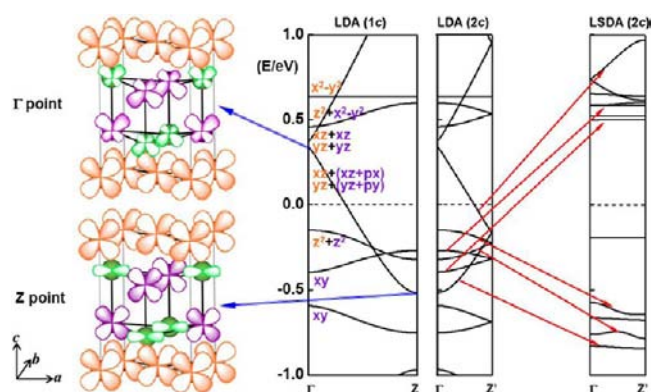


Figure 7. Electronic band structure plots near the Fermi level along Γ -Z, $\Gamma = (0, 0, 0)$; $Z = (0, 0, \pi/c)$, on the Brillouin zone boundary of Mn_2As . (Left) Nonspin polarized (LDA) bands for the crystallographic unit cell (1c) (major d-orbital contributions from Fe1 (orange) and Fe2 (purple) are noted); (Middle) Nonspin polarized (LDA) bands for the unit cell doubled along the c -axis (2c), $Z' = (0, 0, \pi/2c)$; (Right) Spin polarized (LSDA) majority/minority spin bands for the unit cell doubled along the c -axis (2c). Shifts in energy between LDA(2c) and LSDA(2c) bands are indicated by the red arrows. A depiction of the crystal orbitals at the Γ and Z points of the band intersected by the Fermi level is included. The orbital at the Γ point is Mn1 xz (37%), Mn2 $xz+p_x$ (7%), and As $xz+p_x$ (3%). The orbital at the Z point is Mn1 xz (32%), Mn2 xz (14%), and As p_x (2%).

doubly degenerate crystal orbital that involves xz/yz orbitals on both the Mn1 sites and the Mn2 sites. The direct Mn2–Mn2 orbital interactions are significant, as revealed by this COHP curve in Figure 6, although the nearest neighbor Mn2–Mn2 distance is slightly above 3.4 Å. The Fermi level intersects the Mn2–Mn2 COHP curve at nonbonding states, which indicates potential AFM coupling. Doubling the unit cell of Mn₂As along the c -axis, which creates folded bands along c^* , does not reveal any special band or wavevector feature where the Fermi level crosses the resulting bands. But, upon spin polarization as in Fe₂As, the Fermi level falls in the midst of a ~ 0.7 eV energy gap. This band splitting that results from spin polarization involves the xz , yz , and z^2 orbitals on the M1 sites, as well as xy , xz , yz , and z^2 orbitals on the M2 sites, which suggests a combination of Mn2–As–Mn2 superexchange interactions and Mn2–Mn2 direct exchange mechanisms creating the AFM coupling between nearest neighbor Mn2 sites (see Figure 7, orbital interactions at Γ and Z points). We hypothesize that this combination of exchange coupling mechanisms leads to the large effective exchange parameter (-19.6 meV) for the Mn2–Mn2 interaction.

The large unit cell volume for Mn₂As as compared to those of Fe₂As and Cr₂As suggests a greater degree of electron localization in Mn₂As than in the other two arsenides because all interatomic distances will be significantly increased. Moreover, the experimental magnetic moments associated with the two inequivalent Mn sites are nearly equal and much larger than the results of calculations.¹² To explore this possible discrepancy between LSDA calculations and experiment, we included an on-site Hubbard-type orbital repulsion term and carried out LSDA+U calculations³⁷ of the two low-energy magnetic structures, models AF3 and Fi in Figure 3, using VASP. Figure 8 illustrates the variations in relative total

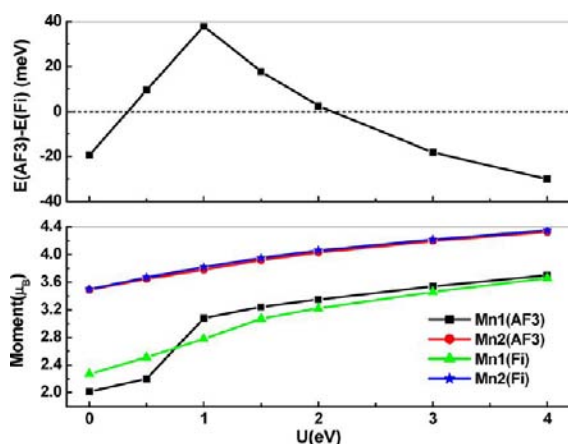


Figure 8. (Top) Energy difference between AF3 and Fi magnetic structures as a function of U for Mn₂As. (Bottom) Magnetic moment variation as a function of U for Mn₂As with AFM and Fi magnetic ordering.

energies and local magnetic moments at the Mn1 and Mn2 sites as a function of the U -parameter from 0 to 4 eV. Somewhat surprisingly, the AFM ground magnetic state (AF3 in Figure 3) is preferred only for small (zero) and large (exceeding 2 eV) Hubbard-type U -parameters. As expected, the local magnetic moments increase monotonically with increasing U , with the greatest effects observed at the Mn1 sites. Nonetheless, all calculations indicate that the local moment

assigned to the Mn1 site will be lower than that at the Mn2 site. Therefore, a reassessment of the magnetic structure and refinement of local moments in Mn₂As seem to be warranted to resolve these discrepancies between theory and experiment.

Cr₂As. As in the LDA DOS curve for Fe₂As and Mn₂As, the Fermi level of Cr₂As lies on a peak (see Figure 9). From the

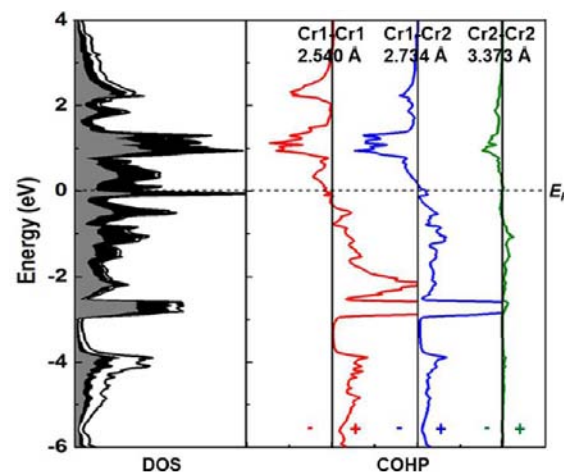


Figure 9. Nonspin-polarized DOS (gray, black, and white represent Cr1, Cr2, and As, partial DOS, respectively) and COHP curves for nearest neighbor Cr1–Cr1 (red), Cr1–Cr2 (blue), and Cr2–Cr2 (green) in Cr₂As. The Fermi level is indicated by the dashed line. + and – signs indicate bonding and antibonding interactions, respectively.

nearest neighbor Cr1–Cr1 and Cr1–Cr2 COHP curves, this energy corresponds to the crossing point from bonding to antibonding states. Although this scenario from the nonspin-polarized electronic structure would suggest AFM coupling for the Cr1–Cr1 and Cr1–Cr2 interactions upon spin-polarization, these two exchange interactions cannot be satisfied simultaneously, as we have seen for Mn₂As. As a result, there are four low-energy magnetic structures for Cr₂As obtained from VASP total energy calculations: (i) AF10, the calculated ground state, which adopts an orthorhombic magnetic space group; (ii) AF7 (+2.2 meV/f.u.), which remains tetragonal; (iii) AF8 (+9.5 meV/f.u.), which is also tetragonal; and (iv) AF5 (+13.7 meV/f.u.), which is orthorhombic. All four magnetic structures have FM Cr1–Cr1 coupling, but both FM and AFM Cr1–Cr2 interactions. The two lower energy magnetic structures show FM nearest neighbor Cr2–Cr2 coupling along the c -axis, whereas these interactions are AFM in the two higher energy cases. Three of these four magnetic structures (AF10, AF7, and AF8) require a doubled crystallographic c -axis.

The effective nearest neighbor Cr–Cr exchange parameters in the ground state AF10 structure were calculated to be AFM for both Cr1–Cr1 (-14.1 meV) and Cr1–Cr2 (average: -10.3 meV). However, as mentioned above, the exchange coupling for Cr1–Cr1 and Cr1–Cr2 contacts cannot be simultaneously AFM, which results in magnetic frustration, as seen by the triangle of two Cr1–Cr2 interactions and one Cr1–Cr1 interaction in Figure 10a. The effective exchange parameter between two Cr2 sites connected through the square net of Cr1 atoms is -6.02 meV, see Figure 10b, which indicates significant AFM coupling between these Cr2 atoms. To satisfy this second nearest neighbor Cr2–Cr2 AFM coupling, the Cr1–Cr1 exchange is AFM, whereas mixed exchange occurs for the

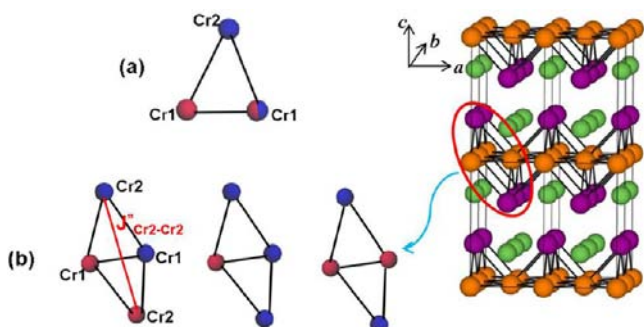


Figure 10. (a) Spin frustration in the Cr1–Cr2–Cr1 triangle (red and blue colors represent spin-up and spin-down orientations). (b) Possible arrangements of magnetic moments in one unit cell of a layer of short Cr–Cr contacts (see Figure 1).

Cr1–Cr2 contacts, that is, Cr1–Cr2 adopts AFM coupling along the *a*-axis, but FM coupling along *b*-axis. Therefore, the stability of the magnetic ground state of Cr₂As may be attributed to indirect Cr2–Cr2 AFM coupling across the square net of Cr1 atoms.

Simulations of neutron diffraction patterns were evaluated for the four lowest energy magnetic structures, AF5, AF7, AF8, and AF10, using the General Structure and Analysis System (GSAS) program.³⁸ A wavelength of 1.599 Å was chosen for the simulation to compare directly with the experimental neutron diffraction pattern.³⁹ All magnetic moments were chosen to lie in the *ab*-plane.³⁹ Among these four simulated patterns, which are shown together with the experimental pattern in Supporting Information, Figure S5, none adequately match the experimental neutron diffraction results in terms of peak positions and relative intensities. In the experimental pattern, there is a strong (00^{1/2}) peak, and the (100) peak is much stronger than the (10^{1/2}) peak. For AF7 and AF10 models (the two lowest energy ones), the strong (00^{1/2}) peak fits the experimental results, but the (100) peak is much weaker than the (10^{1/2}) peak. For AF5 and AF8 models, the (100) peak is much stronger than (10^{1/2}) peak, which fits this aspect of the experimental results. However, in these cases no (00^{1/2}) peak occurs. So, the true magnetic ground state may be a combination of (some of) these four lowest energy magnetic structures (AF5, AF7, AF8, and AF10), a result which would lead to a complex, noncollinear magnetic ordering pattern. In our opinion, further neutron diffraction studies are needed to elucidate the magnetic structure of Cr₂As.

Magnetostrictive Phase Transition in Cr₂As. In the magnetic ground state of Cr₂As (Figure 2), the nearest neighbor Cr1–Cr2 exchange interaction is AFM along the *a*-axis, but FM along the *b*-axis, an outcome which leads to an orthorhombic magnetic space group. This magnetic coupling could cause a magnetostrictive, orthorhombic distortion of the tetragonal crystallographic structure of Cr₂As, a distortion that could be observed at low temperature or under a magnetic field. To identify whether a possible magnetostrictive distortion in Cr₂As could stem from an instability in the electronic structure, the difference between the charge densities of the spin-polarized and nonspin-polarized electronic structures, $\Delta\rho = \rho(\text{LSDA}) - \rho(\text{LDA})$ was calculated for Cr₂As and is plotted for the *ac*- and *bc*-planes in Figure 11. $\Delta\rho$ evaluated in these two planes clearly differ, although the atomic positions observe tetragonal symmetry, a result which indicates an instability of the tetragonal structure. Geometry optimization was applied to

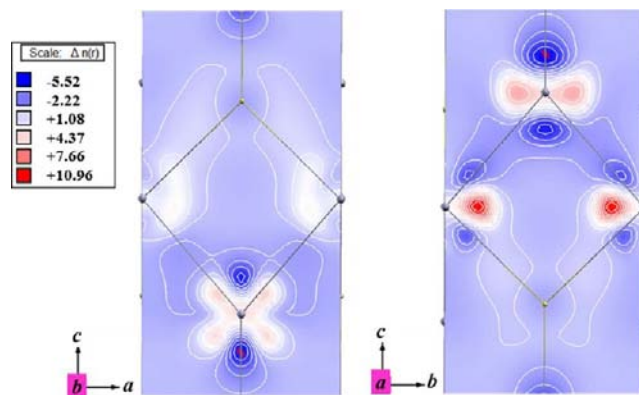


Figure 11. Contour plot of the quantity $\Delta\rho = \rho(\text{LSDA}) - \rho(\text{LDA})$ evaluated in the *ac*- and *bc*-planes of Cr₂As. The large ball and small ball represent the Cr and As atoms, respectively. White lines indicate the zero value contour regions. The color changes from red to blue represent the $\Delta\rho$ range from +10.96 and $-5.52 \text{ e}^-/\text{\AA}^3$.

the magnetic ground state of Cr₂As (AF10) resulting in changes of the unit cell parameters from tetragonal, (see Supporting Information, Table S3), $a = b = 3.592 \text{ \AA}$, to orthorhombic, $a = 3.612 \text{ \AA}$, $b = 3.576 \text{ \AA}$. LDA band structure plots of the tetragonal structure and the optimized, orthorhombic structure (see Supporting Information, Figure S6) indicate a degeneracy breaking in the band structure at the *S* point ($\pi/a, \pi/b, 0$) of the orthorhombic structure compared with the *M* point ($\pi/a, \pi/a, 0$) of the tetragonal structure drives the tetragonal-orthorhombic phase transition.

In fact, a tetragonal-orthorhombic transformation has been observed by Yu et al.⁴⁰ using high pressure powder X-ray diffraction. However, the changes in lattice constants reported by Yu et al. are too large to be driven solely by magnetostriction because the difference between the orthorhombic *a* and *b* lattice constants is about 1 Å. Underlying causes for this distortion of tetragonal Cr₂As remain to be ascertained by quantum chemical calculations.

5. CONCLUDING REMARKS

First-principles calculations were employed on the tetragonal Cu₂Sb-type 3d metal arsenides Cr₂As, Mn₂As, and Fe₂As, to describe the changes in electronic and magnetic structures as a function of the metal atom. Total energy calculations using VASP confirmed the magnetic ground states to be AF10 for Cr₂As, AF3 for Mn₂As, and AF4 for Fe₂As (see Figure 3). Effective exchange parameters (J_{ij}) for nearest-neighbor and next-nearest-neighbor metal–metal contacts were obtained from SPRKKR calculations and show that both indirect and direct exchange couplings play essential roles in understanding the different magnetic orderings observed among these compounds. In effect, the AFM ground states of Fe₂As and Mn₂As result from AFM M2–M2 interactions. These arise by a Fe2–As–Fe2 indirect, that is, superexchange, mechanism in Fe₂As, but by a combination of Mn2–As–Mn2 superexchange and Mn2–Mn2 direct exchange in Mn₂As. The overall magnetic structure of Cr₂As, however, and of Mn₂As as well, is a result of magnetic frustration.

The direct exchange couplings are rationalized using a COHP analysis of the through-space orbital interactions, and show that the M1–M1 and M1–M2 coupling changes from AFM to FM with an increase in the valence electrons count from 17 (Cr₂As) to 21 $\text{e}^-/\text{f.u.}$ (Fe₂As). Thus, the COHPs of direct

metal–metal interaction seem to show “rigid-band” character. To validate this somewhat surprising conclusion, an evaluation of relative total energies of various magnetic structures (see Figure 3) over the range of valence electron counts 17–21 e⁻/f.u. using the DOS curve calculated for Mn₂As yields excellent agreement with experiment and the VASP results, as shown by the energy variations in Figure 12. The FM structure never

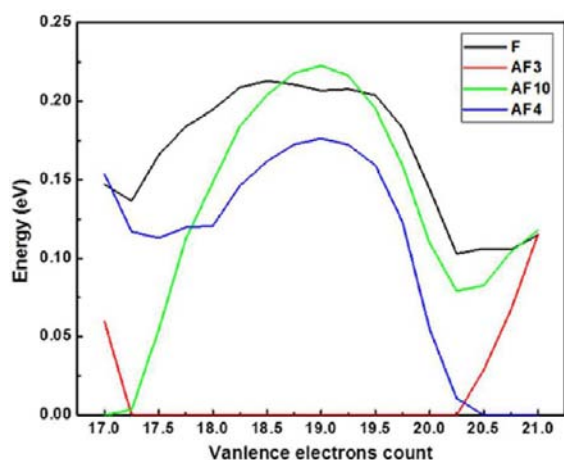


Figure 12. Energy changes as a function of valence electrons count (VE).

competes energetically with the three observed AFM structures. Ternary analogues, for example, MnFeAs and CrMnAs, show different results, however, than predicted by this rigid-band analysis because the chemical differences involving mixed transition metals substantially perturb the 3d contributions to the DOS curves, as we will present in a forthcoming article.⁴¹

All computational results suggest that the local magnetic moments at the M1 sites are consistently smaller than those at the M2 sites, a result which arises from greater M1-M1 orbital overlap than M1-M2 and M2-M2 overlap. Such relative orbital interactions are evident in the Mn1/Mn2 DOS ratio plotted vs energy in Figure 6 (middle). States surrounding the Fermi levels for these three arsenides are weighted toward the M2 sites, whereas M1 sites show enhanced DOS contributions well below (M1-As and M1-M1 bonding) and above (M1-As and M1-M1 antibonding) this region. Furthermore, an examination of Mn₂As using a local on-site Hubbard-type repulsion for electron pairing indicates qualitatively better agreement with experiment regarding large magnitudes of magnetic moments, but the relationship between moments at the M1 and M2 sites remains. In the case of Cr₂As, there are four energetically competing magnetic structures, with the ground state showing AFM Cr1–Cr2 coupling along the *a*-axis, but FM coupling along the *b*-axis. Since none of the four lowest energy magnetic structures, that is, AF5, AF7, AF8, or AF10, seems to be the magnetic ground state according to neutron diffraction simulations, Cr₂As may adopt a complex nonlinear arrangement of magnetic moments. If the differential AFM/FM coupling is maintained along the *a*- and *b*-axes by layers stacked along the *c*-direction, a magnetostrictive tetragonal-to-orthorhombic distortion is predicted to occur in Cr₂As.

■ ASSOCIATED CONTENT

📄 Supporting Information

Further details are given in Tables S1–S2 and Figures S1–S6. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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