Volume 9, Number 1 January, 2000
1009-1963/2000/09(01)/0055-06 CHINESE PHYSICS © 2000 Chin. Phys. Soc.

AB INITIO STUDY ON THE ELECTRONIC STRUCTURE AND MAGNETISM OF MnAs, MnSb, AND MnBi*

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(Received 16 May 1999)

We report the results of first-principles calculations on the electronic structure in ferromagnetic and non-magnetic hexagonal MnV (V=As, Sb, Bi). The calculations are based on the local-spin-density approximation (LSDA) of the density-functional theory (DFT) as well as the atomic sphere approximation (ASA) in the linear muffin-tin orbitals (LMTO) method. For the non-spin-polarized case, the calculated bands in these compounds exhibit p-d mixing in the vicnity of Fermi energy and the Mn 3d bands dominate the antibonding parts of p-d hybride. The spin-polarization in ferromagnetic states are mainly due to the splitting of anti-bonding bands from p-d mixing. The calculated spin moments in these compounds agree fairly well with experimental values and refine previous band calculations. In the spin-polarized band structure, the Mn 3d electrons are found to exhibit week dispersions.

PACC: 7125C; 7510L; 7520E; 7530

I. INTRODUCTION

Transition-metal compounds form a wide group of solids that exhibit various magnetic and electrical properties. MnV (V=As, Sb and Bi) is a group of ferromagnets with the same crystalline structure. As low temperatures, they all exhibit ferromagnetic ordering but with different spin directions. During the past they have drawn both experimental and theoretical efforts due to the unique property displayed by each compound. For MnAs crystal the NiAs structure exists in both high and low temperatures, and transforms into the MnP structure in a limited temperature range from 307—317 K to 393 K. Neutron-diffraction studies by Zieba[1] showed that the NiAs-type ferromagnetic phase is retained down to 4.2 K with the magnetic moment $\mu_{\rm Mn} = 3.31\,\mu_{\rm B}$, and $\mu_{\rm Mn}$ decreased to $2.46\,\mu_{\rm B}$ at 298 K. In the paramagnetic region of NiAs phase, i.e., above $T_{\rm D} = 394$ K, the Curie-Weiss law is obeyed with $\mu_{\rm eff} = 4.45\,\mu_{\rm B}$ and $\theta_{\rm p}$=285 K, which corresponds to $2S = 3.6$. MnSb is s ferromagnet with $T_{\rm c}$=588 K.[2] The magnetic moment in the ferromagnetic regime is $\approx 3.5\,\mu_{\rm B}$ at 77 K with the magnetization perpendicular to the c axis.[3] The spins are parallel to the c axis just below the Curie point, but turn to be prependicular to the c axis at 520 K. Markandeyulu and Rama Rao[4] measured the magnetocrystalline anisotropy above 300 K in single crystals using ferromagnetic resonance (FMR). At 300 K, they found $K_1 = -130\,{\rm kJm^{-3}}$ and K_2=75 kJm^{-3}. Both anisotropy constants pass through zero and change sign at the spin-flip transition of 520 K. At 564 K, the values are $K_1 = 9.8\,{\rm kJm^{-3}}$ and $K_2 = -4.4\,{\rm kJm^{-3}}$. In a study of the pseudobinary system (Cr, Mn)Sb, Reimers *et al.*[5] reported $T_{\rm c}$=573 K for MnSb with a saturation moment of $3.5\,\mu_{\rm B}$ at 0 K. Neutron-diffraction studies of $Mn_{1+t}Sb$ with some excess Mn content have been reported by Watanabe *et al.*[6] MnBi with the NiAs structure is also a ferromagnet in its low-temperature phase (LTP). By varying the temperature, MnBi reveals a series changes in structure and magnetism.[7—9] The saturation moment extrapolated to 0 K was found to be $3.95\,\mu_{\rm B}$. The magnetic moment of Mn is $4.5 \pm 0.2\,\mu_{\rm B}$ at 4.2 K in the ferromagnetic structure. The magnetic c axis anisotropy at higher temperature decreases with temperature and changes sign at 90 K, where the spins turn to a direction in the hexagonal plane.[10]

Band structure calculations of MnAs and MnSb have been made by two different methods: a self-consistent augmented plane wave (APW)[11] method and a recursion calculation.[12,13] Coehoorn *et al.*[14] have preformed spin-polarized band structure calculations for MnSb and MnBi by using the self-consistent (ASW) method. However, the calculations of Motizuki *et al.*[11] were only performed for the assumed non-magnetic states of hexagonal MnAs and MnSb. Their results are insufficient to fully account for the properties of magnetic MnSb. The calculations by Podloucky[12,13], which suffer from certain intrinsic limitations of being an emperical method, cannot describe the megnetism of MnAs and MnSb in their entirety.

In this article, we will report the first-principle calculations of band structure for magnetic as well as non-magnetic MnV (V=As, Sb, Bi). This approach is based on the local spin density approximation (LSDA)[15] of the density function theory (DFT).[16] The calculation method is the linear-

* Project supported by the National Natural Science Foundation of China (Grant No. 19874053) and by the Natural Science Foundation of Zhejiang Province of China (Grant No. 197023).

muffin-tin-orbitals (LMTO) method[17] with scalar relativistic corrections. We will present the band structures for both the spin-polarized and non-spin-polarized cases. We will also compare our results with experiments and previous calculations.

Ⅱ. COMPUTATIONAL METHOD

The electronic ground state of magnetic and non-magnetic MnV (V=As, Sb, Bi) are computated using the relativistic LMTO scheme.[17] The valence states in our claculations are Mn(4s,4p,3d), As(4s,4p), Sb(5s,5p), and Bi(6s,6p), where the frozen-core approximation has been applied to the tightly bound core levels. In our calculations, the one-center expansion of charge density is expanded up to $l_{\max} = 4$. The Fermi level is determined by the Brillouin zone (BZ) integration technique[18]. In particular, in the LMTO method using atomic-sphere approximation (ASA) with $\kappa^2 = 0$, only nine orbitals per atom are typically needed to reproduce energy bands with an accuracy better than 1 mRyd. As for the details of LMTO method, the readers can refer to Ref.[17]. The form chosen for the exchange-correlation energy and potential is that of von Barth and Hedin.[19]

The NiAs-type crystal of the hexagonal space group D^4_{6h} has a unit cell containing two metal atoms and two anion atoms. The corresponding first Brillouin zone is also hexagonal. The lattice constants and muffin-tin radii we chose for the self-consistent calculations in the three compounds of NiAs structure are experimental values (see Table 1). We have calculated the spin-polarized and non-spin-polarized electronic bands for MnV (V=As, Sb, Bi) to an accuracy better than one part per million in charge density and 10^{-6} Ryd in total energy. The density of states (DOS) has been computed using the energy eigenvalues determined at 1524 $\boldsymbol{k}$ points in the 1/24 Brillouin zone.

Table 1. Lattice parameters and muffin-tin radii used in band calculations.

Compound	MnAs	MbSb	MnBi
a/nm	0.372	0.412	0.4285
c/nm	0.572	0.578	0.6113
Muffin-tin radii/a.u.	$R_{\rm Mn} = 2.57$, $R_{\rm As} = 2.83$	$R_{\rm Mn} = 2.57$, $R_{\rm Sb} = 3.30$	$R_{\rm Mn} = 2.57$, $R_{\rm Bi} = 3.37$

Ⅲ. CALCULATED RESULTS

A. Non-spin-polarized case

We show the band structures along the symmetry lines in Brillonin zone and DOS curves for non-magnetic MnV (V=As, Sb, Bi) in Figs.1 and 2,

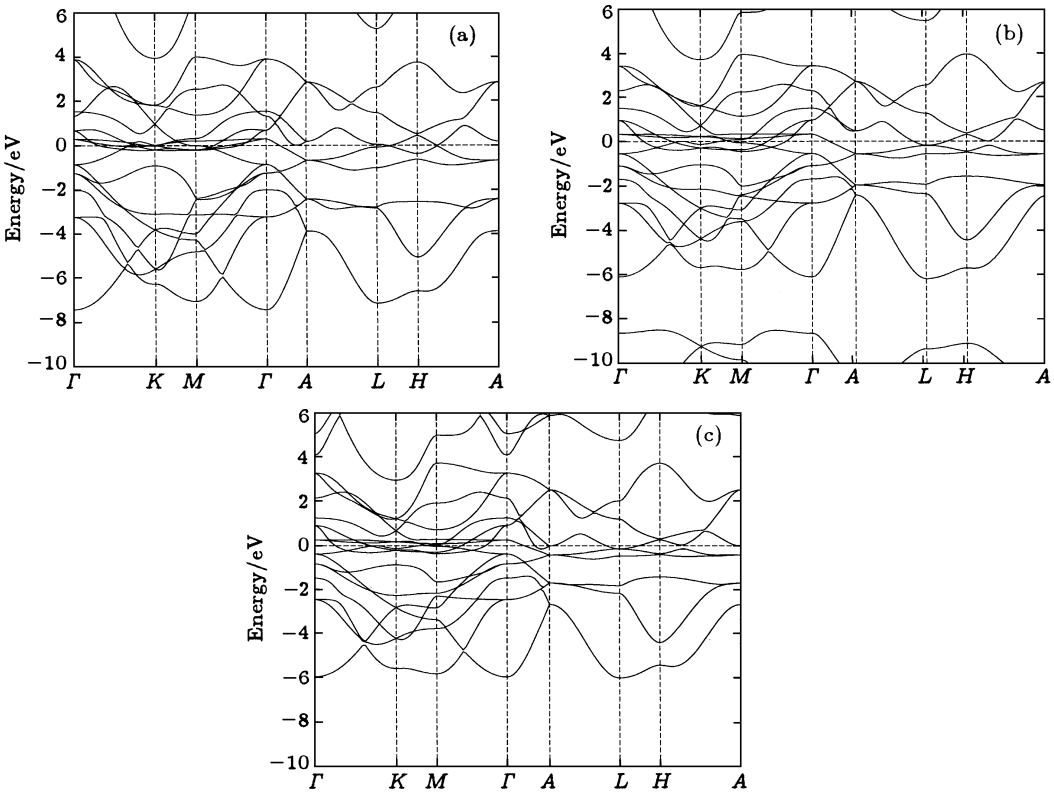


Fig.1. Band structures of non-spin-polarized MnV. (a) MnAs; (b) MnSb; (c) MnBi.

respectively. It is obvious that the lowest valence bands should be ns of As, Sb and Bi. The ns bands of MnAs and MnBi are not shown because they are located well below 10 eV from the Fermi level. The bands in the vicinity of the Fermi level E_F are mainly derived from the hybridization of Mn 3d and V np bands. As shown in the figures, the density of states of d-p hybride consists of two parts: (a) in the lower energy side and (b) in the higher energy side, arising from the bonding and anti-bonding p-d mixing bands, respectively. The DOS at E_F are calculated to be 174, 144 and 120 (states/Ryd-unit cell) for MnAs, MnSb, and MnBi, respectively. These values are very close to that reported by Motizuki *et al.*[11] From Stoner argument it is easy to conclude that such large DOS values at E_F are favourable for the ferromagnetic states to stabilize.

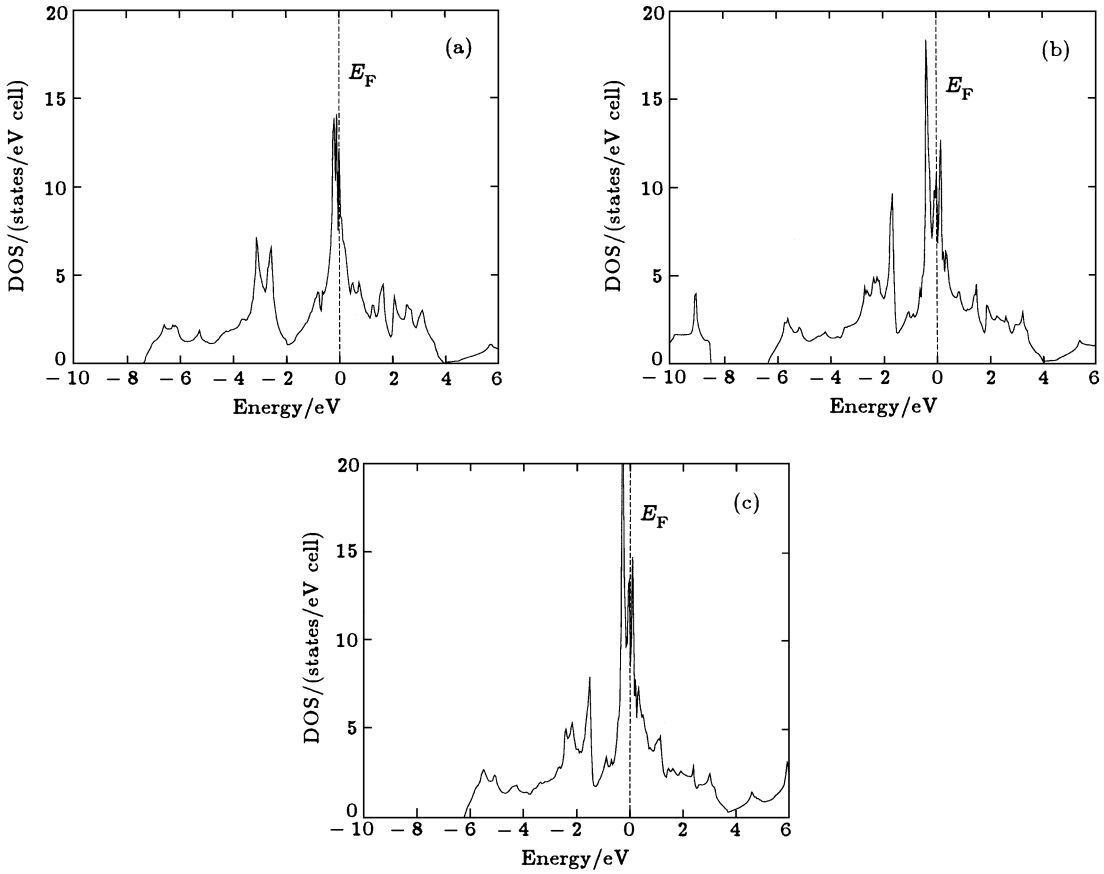


Fig.2. DOS for non-spin-polarized MnV. (a) MnAs; (b) MnSb; (c) MnBi.

B. Spin-polarized case

In this section, we present the result of our calculation on the spin-polrized band structure in MnV. In Table 2, the calculated spin moments in MnV are compared with the available experimental results. For MnAs and MnSb, our LSDA predictions on spin moments agree fairly well with experiments. There are two diversely different values of the spin moments measured in MnBi, i.e., $3.95\,\mu_B$ and $4.5 \pm 0.2\,\mu_B$. Our LSDA calculations indicate that the former value is more reasonable. Our calculated spin moments for MnV are systematically lower than experimental values. For comparision, we found in literature that Motizuki[20] calculated the total magnetic moments for MnAs and MnSb to be $3.1\,\mu_B$/f.u. and $3.2\,\mu_B$/f.u., respectively. In the ASW calculation by Coehoorn *et al.*[14], the total spin moment for MnSb is $3.24\,\mu_B$/f.u. These results agree fairly well with our results. In a recent article[21] on magneto-optical Kerr effect in MnBi and related compounds, the spin moment of MnBi is $3.61\,\mu_B$/f.u., a similar value as ours.

Table 2. Spin moments in MnV compounds.

	Calculated moment/μ_B	Experimental moment/μ_B
MnAs	3.16	3.31
MnSb	3.34	3.5 ± 0.1
MnBi	3.66	$3.95\,\&\,4.5 \pm 0.2$

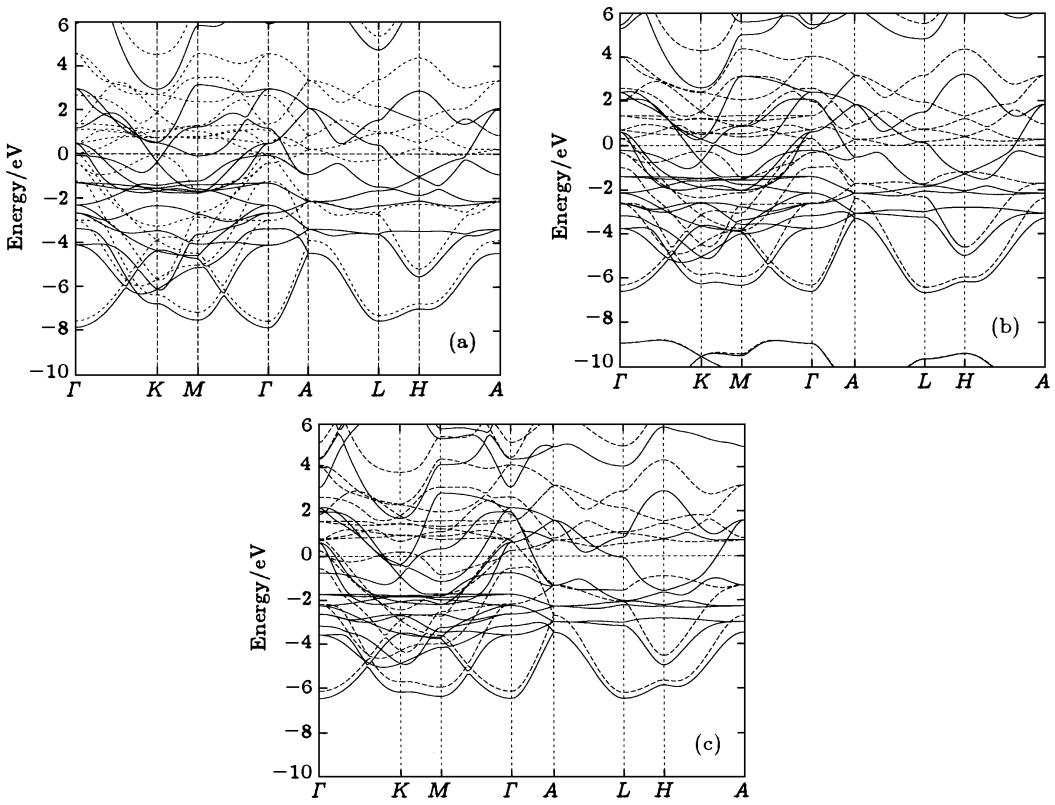


Fig.3. Band structures of spin-polarized MnV. Solid lines: majority bands; dashed lines: minority bands. (a) MnAs; (b) MnSb; (c) MnBi.

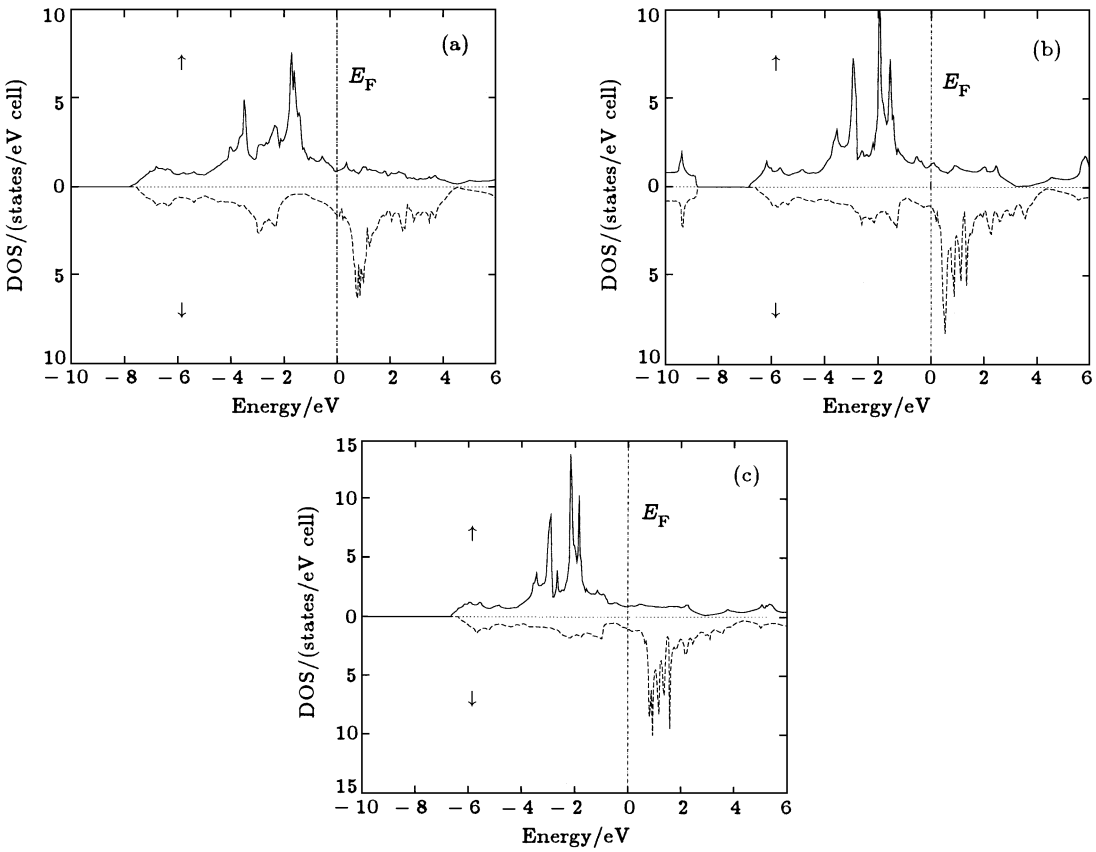


Fig.4. DOS for spin-polarized MnV. Solid lines: majority bands; dashed lines: minority bands. (a) MnAs; (b) MnSb; (c) MnBi.

For MnSb and MnBi, the quantization axis in the ground state are [100] and [001] respectively. The spin directions will change at characteristic temperatures. This reflects that there exists strong spin-orbital coupling (SOC) in addition to the usual spin polarization in MnSb and MnBi. Because the code we used in this work dose not include spin-orbital coupling, we are unable to estimate the effects of SOC on the spin moments. This problem deserves further study.

In Figs.3 and 4 we show the spin-polarized band structures and DOS of ferromagnetic MnV. In Fig.4, one can see that the spin-polarization is mainly from the splitting of p-d mixing bands near the Fermi level. The ns bands formed by atomic V contribute almost nothing to the spin splitting. Another important conclusion can be draw from Figs.3 and 4 is that the DOS at $E_{\rm F}$ in the spin-polarized MnV are smaller than that of non-spin-polarized MnV. In fact, these compounds display almost the same features in their energy band structures. This similarity comes from the common crystalline structures.

IV. DISCUSSIONS

Several models have been proposed for the magnetic properties of metallic solids. In the Stoner model of band magnetism, the electrons and the magnetic moments are itinerate, and the exchange splitting of the energy bands below $T_{\rm c}$ leads to the ferromagnetic properties. This band model has been applied to transition metals, and in particular to weak magnetic compounds such as $ZrZn_2$. In the Heisenberg model one assumes the presence of localized electrons and magnetic moments as a consequence of strong correlations among electrons. This description has also been applied to transition metals, and it is valid in particular for the strongly localized magnetic moments in rare-earth metals. The nature of magnetic moments in strongly covalent transition-metal compounds has been discussed by Kübler *et al.*[22] These authors found that the electrons are delocalized, but the magnetic moments are strongly localized on the transition-metal atoms. This is just the case in MnSb.[23,24] It can be seen from Figs.3 and 4 that the local moments in MnV are responsible for the weak dispersion in Mn d bands. In this sense, MnV can be classified as local-moment metals.

It should be noted that in the local-moment metals such as MnV, the correlation between d band electrons are stronger than that in pure transition metals. This is also the reason why the calculated moments are systematically smaller than experimental values. We suspect that if some improvements beyond plain LDA had been made, the theoretical calculations would result in more reasonable values. In this aspect, LDA+U and SIC-LDA have set up excellent examples for us. For the intermetallic systems containing transition metal atoms, it seems optimistic to calculate with the plain LSDA scheme. Although d band electrons are correlated in these compounds, the interactions between them are still well screened because of the presence of a well developed conduction band, where Thomas-Fermi screening applies. This situation is just opposite to the case of insulating transition metal oxides, namely Mott-Hubbard insulators. Because of the intrinsic disadvantage of LSDA, some patched approachs to LSDA such as SIC-LSDA[25] and LDA+U[26] have been proposed. Some improved results on band gap and spin moment beyond LSDA have been obtained.

V. CONCLUSION

In summary, we have studied the band structures of MnV (V=As, Sb, Bi) by ab initio LMTO-ASA method in order to calculate the energy bands and magnetic spin moments in these compounds. Our calculated results show that the assumed non-spin-polarized electronic bands in all three compounds exhibit strong Stoner instability due to the rather high DOS at $E_{\rm F}$. The bands near $E_{\rm F}$ are mainly from the hybridization of Mn 3d states and V np states. In the spin-polarized states, the spin-polarization comes from the exchange splittings of p-d mixed bands. Our calculated spin moments for the compounds agree fairly well with experimental results and are consistent with previous self-consistent band structure calculations. The d bands in the three compounds exhibit strongly localized characteristics, supporting the picture of a local-moment metal.

ACKNOWLEDGEMENT

The first author would like to thank the Pao Yu-kong and Pao Zhao-long Scholarship for Chinese Students Studying Abroad.

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