Electronic features around Fermi level correlating to occurrence of magnetism or superconductivity in Laves-phase intermetallic compounds

Xing-Qiu Chen\textsuperscript{a}, Shu-Lan Wang\textsuperscript{b}, Xue-Yong Ding\textsuperscript{a}, and Xiang-Xun Xue\textsuperscript{a}

\textsuperscript{a} School of Materials and Metallurgy, Northeastern University, Shenyang 110004, Peoples’ Republic of China, and

\textsuperscript{b} School of Science, Northeastern University, Shenyang, 10004, Peoples’ Republic of China.

Based on density functional calculations, the relationship between magnetism or superconductivity and electronic states around Fermi level were derived, and the location of the Fermi level in nonmagnetic “form” of Laves-phase compounds is very sensitive to determine the presence of nonmagnetism, or ferromagnetism, or antiferromagnetism, or superconductivity. The Fermi level at the nonbonding and antibonding regions corresponds for the nonmagnetism and magnetism, respectively, whereas at bonding region with responsibility for superconductivity. This rules will be very useful and convenient to search the new magnetic and superconductive materials.

The searches of new magnetic and superconductive materials have always simulated extensively interesting in materials science. As we know, a precise location of $E_F$ is very important for those physical properties (such as magnetism and superconductivity) which depend critically on the value of the DOS at Fermi level. Generally, in the nonmagnetic phase the higher values the DOS at Fermi level have, the more possible the compound is magnetic or superconductivity. Nowadays, for magnetic systems most solid-state physicists accept the Stoner criterion \cite{1} to decide whether or not a metal or alloy should be ferromagnetic,

$$IN(E_F) > 1 \quad (1)$$

where $I$ is a measure of the strength of the exchange interaction in the metal and $N(E_F)$ is the density of states at Fermi level, $E_F$. As a predictive tool Stoner theory is actually not always successful, for instance, in the first transition metals Fe, Co, Ni are all ferromagnetic, however using Stoner theory for cobalt $IN(E_F) = 0.972 < 1$ \cite{2} which indicated Co should be nonmagnetic; It is even also somewhat strange that nickel, the weakest ferromagnetic, has the largest value $IN(E_F) \approx 2.0$ \cite{3}. On the other hand, for superconductive materials a basic ingredient in theories evaluating the superconducton transition temperature is the electron-phonon interaction \cite{4}. The strength of this interaction is conveniently expressed by $\lambda$, the electron-phonon coupling parameter,

$$\lambda = \frac{N(E_F) < I^2 >}{M < \omega^2 >} \quad (2)$$

where $< I^2 >$ is the electronic stiffness parameter of Gaspari and Gyorffy \cite{5}, $M$ the ionic mass, and $< \omega^2 >$ some mean value of the phonon frequency. From the above equations we have deliberately used definitions from the simplest available electronic theories for magnetism and superconductivity, just to stress the relevant role played in these phenomena by $N(E_F)$. For example, HIV$_2$, with high DOS of V atom satisfying the Eq.\cite{11} is nonmagnetic superconductive materials. Then, at least high DOS at Fermi level does not guarantee the occurrence of ferromagnetism or superconductivity. Therefore, it is very necessary to pursue the more reliable tool to estimate whether or not a material is ferromagnetic, or antiferromagnetic, or superconductivity. For this point, in 2000 Landrum and Dronskowskii \cite{6} made the first work – they thought whether or not an alloy contains ferromagnetic elements, the presence of antibonding states at $E_F$ serves as a “fingerprint” to indicate a ferromagnetic instability.

In this Letter, we present an understanding for occurrence of magnetism or superconductivity in Laves-phases compounds by the electronic states around Fermi level. Laves phase compounds, the largest class of intermetallics, have a wide interesting physical and technological properties in particular for magnetism, superconductivity, and hydrogen storage \cite{7,8,9}. Many of these compounds crystallize in the densely packed hexagonal C14 and C36, and the cubic C15 crystal structures \cite{10}. Searching for the ground state structure of Mn-, Fe-, Cr-, V-based binary transition-metal Laves phases (total 16 compounds) we performed density functional calculations for the C14, C15 and C36 structures finding many new and interesting magnetic ground and metastable states \cite{11}: for Mn-based Laves phases, ScMn$_2$, YMn$_2$, and LuMn$_2$ crystallize in C15 antiferromagnetic (AF) ground states, and TiMn$_2$ \cite{12}. HfMn$_2$ and NbMn$_2$ have C15 ferromagnetic (FM) metastable states, and ZrMn$_2$ stabilizes the C15 FM with near-degeneracy of C15, C14, and C36 phases at ground state \cite{13}. For TiFe$_2$, ZrFe$_2$, and HfFe$_2$, all of them crystallize C15 FM ground states; RCr$_2$ and RV$_2$ (R=Ti, Zr, Hf) have all C15 nonmagnetic (NM) ground states. When we analyzed the electron states of these C15 stable or metastable Laves phases, a principle can be found for NM, AF, FM, and superconductivity. This new finding is the subject of our paper.

For the calculation of ground state properties of these above mentioned Laves phase compounds in the C14, C15 and C36 crystal structures we applied density functional theory (DFT) by means of the plane wave Vienna Ab initio Simulation Package (VASP)\cite{14} which –in its projector augmented wave formulation- is one of the most precise methods for calculating the energetics and electronic structure of solid matter within periodic boundary conditions. For the many-body exchange-correlation interaction the generalized gradient approximation of Perdew and Wang \cite{15} in combination with the approach of Ref. \cite{16} for spin polarization was chosen. The calculations are free from any empirical parameters. Lattice parameters as
nonmagnetic Laves phase compounds are shown in Fig.1. The total DOS curves (not shown here), which runs from -5 to 7 eV, are mainly composed of d states of both two constituent elements in compound RMn$_2$ (R = Ti, Zr, Hf; M = V, Cr, Fe, Mn). The distinct features for all 16 compounds is that the pronounced pseudogap around Fermi energy occurs separating the energy regions of bonding and antibonding states. A very large peak of unoccupied d-like states of R atoms arises at high energy part above Fermi level which is due to nonbonding states. In compounds RV$_2$ (R=Ti,Zr,Hf) the Fermi level $E_F$ falls in a relative high DOS at down-shoulder of strong R-V bonding region, whereas for RCr$_2$ the Fermi level lies the valley of the pronounced pseudogap with very low DOS values. Clearly, RV$_2$ compounds have relative high DOS at Fermi level, even satisfying Stoner theory. So, one would expect the occurrence of ferromagnetic phases or the instability of structure. However, our spin-polarized calculations revealed that they are nonmagnetic. Furthermore, experiments found that HV$_2$ and ZrV$_2$ are superconductive materials with C15 structures (ZrV$_2$ with $T_{sc}$ = 8.8 K [17]; HV$_2$ with $T_{sc}$ = 9 K [18]). Up to date, no experiment reported C15-type TiV$_2$. The calculated enthalpies of formations of 30.2, -3.6, and -4.5 kJ/mol for TiV$_2$, ZrV$_2$, and HV$_2$, respectively, prove that C15 TiV$_2$ is unlikely to exist thermodynamically due to highly positive formation energy. On the contrary, according to the theory of electronic structure the low DOS value at Fermi level means the stability of system. Therefore, in RCr$_2$ compounds the appearance of $E_F$ in low pseudogap indicates a system is stable with C15 NM phase, which are perfect agreement with experimental investigations [19].

For RMn$_2$ and RF$_2$ compounds, DOS curves are similar to RCr$_2$ and RV$_2$. The important difference is that the Fermi level now lies on the sharp peak of antibonding region. It is also noted that there is an obvious nonbonding region between R-$d$ and Mn-(Fe-)$d$ states below the Fermi level, where d-like states of all R atom have a very flat curves around the pseudogaps (see Fig.1). Actually, our further spin-polarized calculations show that these nonmagnetic C15 RMn$_2$ and RF$_2$ compounds are unstable with respect to an electronic structure distortion. The magnetic calculations revealed that all these compounds have C15 ferromagnetic ground or metastable states (their magnetic properties are given in Table 1), which result in high DOS values in all cases. At the left of the Fermi level there are also pronounced pseudogap with very flat curves of d-like states of Mn atoms shift up to almost make the band fully unoccupied, however the spin-down electrons states must decrease to make more electrons occupy this state. This kind of splitting in energy for spin-up and spin-down states is namely the exchange spin splitting (these values of both RMn$_2$ and RF$_2$ are also given Table1), which result in the occurrence of ferromagnetism for these compounds. Now we still see another important key indications that the Fermi level $E_F$ falls down the valleys (very low DOS, see Fig. 1) of DOS curves in magnetic cases - imply that these compounds can crystallize in C15 FM phases.

| Compounds  | stabilities     | moment (µ$_B$/Fe) | splitting (eV) |
|-----------|-----------------|-------------------|---------------|
| TiMn$_2$  | metastable FM   | 0.76/Mn           | 0.78          |
| ZrMn$_2$  | ground state FM | 0.90/Mn           | 0.94          |
| HfMn$_2$  | metastable FM   | 0.86/Mn           | 0.90          |
| TiFe$_2$  | ground state FM | 1.5/Fe            | 1.56          |
| ZrFe$_2$  | ground state FM | 2.0/Fe            | 2.03          |
| HfFe$_2$  | ground state FM | 1.3/Fe            | 1.32          |
| ScMn$_2$  | metastable AF   | ±1.4/Mn           | 1.42          |
| YMn$_2$   | ground state AF | ±2.6/Mn           | 2.67          |
| LuMn$_2$  | ground state AF | ±2.2/Mn           | 2.22          |

TABLE 1: The stabilities and magnetic properties of C15 RMn$_2$ (R=Sc, Y, Lu; Ti, Zr, Hf) and RF$_2$ (R=Ti, Zr, Hf) Laves phase compounds.

Furthermore, RMn$_2$ (R=Sc, Y, Lu) compounds with C15 Laves phase type are also investigated. The electronic states of them are shown in Fig.2. It is very clear to see that $E_F$ lies in the crossover point between nonbonding and antibonding regions with high DOS values in all cases. At the left of the Fermi level there are also pronounced pseudogap with very flat curves of d-like states of R atoms, and at the right of the Fermi level a relative weak antibonding region begin to appear. Because their DOS values at Fermi level satisfy the Stoner theory, the C15 phases of these compounds should be expected to have ferromagnetic properties as well. Surprisingly, our spin-polarized calculated revealed that their C15 phases are not all ferromagnetism, but antiferromagnetism (local moments are listed in Table1). By spontaneous AF spin
polarization all three compounds gain different magnetization energies defined by $U_{DFT}(AF; V_0) - U_{DFT}(NM; V_0)$ are 2.4, 26.1, and 7.7 kJ/mol with respect to their nonmagnetic states for ScMn$_2$, YMn$_2$, and LuMn$_2$, respectively. Additionally, the happy fact is that for YMn$_2$ our current calculations are well agreement with the recent experimental observations ($2.7 \mu_B$/Mn with C15 AF structure [21]). For ScMn$_2$ and LuMn$_2$ no comparison of magnetic structures is possible due to the lack of experimental measurements. Now we briefly de-
in energy (see Fig. 4) upon the spontaneous spin polarization.

So, now we revived again to note the electronic states of all RM2 Laves phase compounds considered here according to above discussions. There are some important and simply features can be drawn for their nonmagnetic electronic states:

(i) for nonmagnetic Laves compounds, e.g. RCr$_2$ (R=Ti, Zr, Hf), the Fermi level $E_F$ lies in the valley of the pronounced pseudogap;
(ii) for superconductivity Laves compounds, e.g. ZrV$_2$ and HfV$_2$, the Fermi level $E_F$ lies in the bonding region with relative high DOS value;
(iii) for ferromagnetic Laves compounds, e.g. ZrFe$_2$, ZrMn$_2$, etc, the Fermi level $E_F$ lies in the strong antibonding region with very high DOS value (generally sitting at a sharp peak);
(iv) for antiferromagnetic Laves compounds, e.g., RMn$_2$ (R=Sc, Y, Lu), the Fermi level $E_F$ is close to the crossover boundary between nonbonding and antibonding regions also with high DOS values.

Currently, for TiV$_2$ the above analysis indicated that it satisfies the criterion (ii), then it should be superconducting materials. But, as already pointed out, it is a pity that the phase actually is unstable due to highly positive enthalpy of formation. In order to check the reliability of the principles, we also further investigated ZrMo$_2$, NbMn$_2$, and GdMn$_2$ Laves phase compounds with C15 phase. It has been found C15 phase of NbMn$_2$ is metastable and ZrMo$_2$ and GdMn$_2$ have C15 ground state. The electronic structures in the C15 "nonmagnetic" forms are given in Fig. 5. Clearly, it can be seen that the Fermi level $E_F$ of C15 NbMn$_2$ falls on the sharp peak in the strong antibonding region between Nb- $d$ and Mn- $d$ states (satisfying the criterion (iii)). Then the phase should be ferromagnetism. The spin-polarized calculations exactly reveal the point – Mn atom has a moment of 0.6$\mu_B$ in C15 NbMn$_2$; For C15 ZrMo$_2$, the Fermi level lies on the valley of pseudogap where the obvious nonbonding region appears (satisfying the criterion (i)), meaning it should be the stable nonmagnetic phase. The spin-polarized calculations definitely found that it is nonmagnetic; for C15 GdMn$_2$, from Fig. 5 a nonbonding region of Mn- $d$ and Gd- $d$ states exists from -0.6 eV to $E_F$, and at the right side of $E_F$ the antibonding region begin to appear. Namely, the Fermi level $E_F$ exactly sits at the crossover boundary between nonbonding and antibonding regions (satisfying the criterion (iv)). So the compound GdMn$_2$ should have antiferromagnetic property. The spin-polarized calculations revealed that it is an antiferromagnetic structure with local moments of $\pm 2.6$ $\mu_B$ per Mn atom and $\pm 0.4$ $\mu_B$ per Gd atom. From experiments [22] it can be found that the local moments are $\pm 2.1$ and $\pm 4.6$ $\mu_B$ for Mn and Gd atoms, respectively. The difference of the local moment of the calculations and experiments for Gd atom is mainly due to the soft potential (calculating nine valence electrons) of Gd atom applied in the calculations. Normally, I would use the hard potential for Gd (with 18 valence electrons). Unfortunately, VASP does not converge for the hard potential in GdMn$_2$ case.

At last, the emphases should be played on the reliability of predictions in this work. The properties of all these compounds were predicted based on the atomic scale simulations within quantum physical density function theory. Many established facts are the right ground states and phase relation for these compounds are predicted. On the other hand, the calculations of ZrFe$_2$ and YMn$_2$, which are in perfect agreement with experimental results, also further confirmed our results. For all compounds considered here, the obtained the equilibrium lattice constants and lattice parameters are in good agreement with experiment [1][12]. The calculated volume is slightly smaller within 5% due to the approximations made for the many-body term of DFT. Furthermore, the quality of our data is corroborated by the calculated energies of formation which in many cases agree with reliable experimental data, such as TiMn$_2$ [12].

Summarizing, our argument is that the occurrence of magnetism and superconductivity in Laves phase compounds directly depends on the electronic states around Fermi level in their nonmagnetic phase. The basis principles of (i), (ii), (iii), and (iv) have already been established to open the useful clues for searching new magnetism and superconductive materials.

---

[1] E.C.Stoner, Collective electron specific heat and spin paramagnetism in metals, Proc. R. Soc. London A, 1938, 165, 372; Collective electron ferromagnetism II. Energy and specifit heat, Proc. R. Soc. London A, 1939, 169, 339.
[2] J.F.Janak, Uniform susceptibilities of metallic elements, Phys. Rev. B, 1977, 16, 255-262.
[3] G.A.Landrum and R.Dronskowski, The orbital origins of magnetism: from atoms to molecules to ferromagnetic alloys, Angew. Chem. Int. Ed., 2000, 39, 1560-1585.
[4] M.C.Huang, H.J.F.Jansen, A.J.Freeman, Self-consistent full-potential linearized-augmented-plane-wave local-density eletronic-structure studies of magnetism and superconductivity in C15 compounds: ZrZn$_2$ and ZrV$_2$, Phys. Rev. B, 1988, 37, 3489-3496.
[5] G.D.Gaspari and B.L.Györffy, Electron-Phonon interactions, d resonances, and superconductivity in transition metals, Phys. Rev. Lett., 1972, 28, 801-804.
[6] C.Pfleiderer, M.Uhlzar, S.M.Hayden, R.Vollmer, H.v.Löhneysen, N.R.Bemhoeft, and G.G.Lonzarich, Coexistence of superconductivity and ferromagnetism in the
[7] D.J. Singh, I.I. Mazin, Competition of spin fluctuations and phonons in superconductivity of ZrZn2, Phys. Rev. Lett., 2002, 88, 187004.
[8] C. Robert, Jr. Bowman, F. Brent, Metallic hydrides I: hydrogen storage and other gas-phase applications. MRS Bulletin, 2002, 27, 688-693.
[9] J. öble, M. Huth, Correlation of quenched structural disorder and magnetism in TiFe2 Laves-phase thin films, Phys. Rev. B, 2002, 66, 144414.
[10] J. R. Friauf, The crystal structure of magnesium di-zincide, Phys. Rev. 29, 34-40 (1927); F. Laves, In Theory of Alloy Phases (ASM, Cleveland, OH, 1956), pp. 123.
[11] X.Q.Chen, W.Wolf, R.Podloucky, P.Rogl, Density functional study of structural and phase stabilities for RMn2 Laves phases (R=Sc,Y,Ti,Zr,Hf), J. Alloys Compounds, 2004, in press.
[12] X.Q.Chen, V.T.Witusiewicz, R.Podloucky, P.Rogl, F.Sommer,Computational and experimental study of phase stability, cohesive properties, magnetism and electronic structure of TiMn2, Acta Mater, 2003, 51, 1239.
[13] X.Q.Chen, W.Wolf, R.Podloucky, P.Rogl, M.Marsman, A new polymorphic material? Structural degeneracy of ZrMn2,[http://arXiv.org/abs/cond-mat/0403469] Europhys. Lett., 2004, in press.
[14] G. Kresse, D. Joubert, From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B, 1999, 59, 1758-1775.
[15] J. P. Perdew, Y. Wang, Accurate and simple analytic presentation of the electron-gas correlation energy. Phys. Rev. B, 1992, 45, 13244-13249.
[16] S. H. Vosko, L. Wilk, M. Nusair, Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis. Can. J. Phys., 1980, 58, 1200-1211.
[17] B.T. Matthias, V. B. Compton and E. Corenzwit, Some new superconducting compounds, J. Phys. Chem. Solids, 1961, 19, 130-136.
[18] B.Luthi, M.Herrmann, W.Assmus, H.Schmidt, H.Rietschel, H.Wuhl, U.Gottwick, G.Sparn, and F.Steglich, Normal-state and superconducting properties of HfV2, Z.Phys. B, 1985, 60, 387.
[19] T.B.Massalski, Binary Alloy Phase Diagrams, 2nd Edition, ASM international, 1990.
[20] A.T.Motta, G.L.Catchen, and S.E.Cumblidge, Defects and magnetic hyperfine fields in ZrFe2 investigated using perturbed-augular-correlation, Phys. Rev. B, 1999, 60, 1188-1196; A.L.de Oliveira, N.A.de Oliveira, A.Troper, Hyperfine fields at 3d impurities in ZrFe2 intermetallic compound: A theoretical study, J. Appl. Phys., 2002, 91, 8876-8878.
[21] H.Nakamura, N.Metoki, S.Suzuki, F.Takayanagi, and M.Shiga, Helimagnetic structure of YMn2 observed by means of nuclear magnetic resonance and neutron diffraction, J.Phys.: Condens. Matter, 2001, 13, 475-500.
[22] B.Ouladdiaf, C.Ritter, R.Ballou, J.Deportes, Magnetic ordering of GdMn2, Phys. B, 2000, 276-278, 670.