Correlation Induced Paramagnetic Ground State in FeAl

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Experimentally the intermetallic compound FeAl is known to be nonmagnetic, whereas conventional density functional theory calculations within the local density approximation always yield a ferromagnetic ground state with a magnetic moment at the Fe site of about $0.7\mu_B$. We show that a correlation correction within the LDA + U scheme yields a nonmagnetic ground state for $U \geq 3.7$ eV using two different implementations. The disappearance of the magnetic ground state occurs since Fe-t_{2g} and Fe-e_g manifolds are affected differently by a common U. For large values of U a magnetic solution reappears as expected for strong correlation.

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Alloys of iron and aluminum based on B2 FeAl are found to be most versatile materials. They are at least 25% lighter than steel and form, due to their high aluminum content, a protective oxide layer at high temperatures. These alloys are often used as strong, lightweight structural materials in environments vulnerable to sulfidation, corrosion, or oxidation or as heating elements, utilizing their high electrical resistivity. They are resistant to oxidation up to about 1500 K, and their hardness can be increased by 150% through heat treatment. All these properties make this material of great technological importance. Consequently the scientific interest in this alloy has been rather high for the last few decades. Many first principles investigations on the electronic and magnetic structure have been conducted during the past few years to provide a microscopic understanding of the chemical bonding, the formation of clusters, surfaces, phase stability, etc.

In this Letter we focus on the ground state properties of FeAl as determined from first principles calculations of the electronic structure. The alloy system Fe-Al exhibits a rich magnetic structure. Increasing the Fe content above 50%, a reentrant spin glass phase appears at temperatures below 50 K and above 70% ferromagnetism sets in [1]. For Fe concentrations $\leq 50\%$, the alloy is phase separated paramagnetic. An experimental and theoretical study of the magnetic order and the defect structure of Fe_xAl_{1-x} around $x = 0.5$ can be found in Refs. [2] and [3]. For the stoichiometric composition FeAl an intermetallic compound is formed which crystallizes in the CsCl (B2) structure and is *nonmagnetic*.

In contrast to the nonmagnetic state found experimentally all calculations of the electronic structure of FeAl within the local spin density approximation (LSDA) for exchange and correlation always yield a *ferromagnetic* ground state. These results were obtained employing various kinds of band structure codes like the ASW (augmented spherical wave) [4], the FP-LAPW (full potential linear augmented plane wave) [5], the FP-LMTO (full potential linear muffin tin orbital) [6], the KKR (Korringa-Kohn-Rostoker) method [7], or the embedded cluster model [8]. All these methods yield very similar results concerning the magnetic moment M at the Fe site $(0.7\mu_B)$ and the electronic structure, which is discussed in detail in Ref. [3]. If the system is forced to be nonmagnetic the Fermi energy, ε_F, lies in a peak of the Fe density of states (DOS) that consists mainly of d states with t_{2g} symmetry. Because of the large DOS at ε_F, the Stoner criterion is fulfilled and thus a magnetic ground state is more stable than a nonmagnetic one. This feature appears for both the standard LSDA [9] and, even more pronounced, for the gradient corrected (GGA) version [10] of density functional theory (DFT). One also finds that this magnetic state appears to be quite stable over a wide volume range since a reduction of the lattice constant by more than 10% is required to suppress magnetism. It is known that usually LSDA and even more so GGA favor the formation of magnetic order. In the present case, however, the high stability of the magnetic phase suggests that this deviation from experiment must be more fundamental and thus goes beyond the usually

small LSDA error. From the fact that all investigations yield the same magnetic ground state an artifact of a single band structure code can be ruled out. It thus seems more likely that the approximate treatment of exchange and correlation by LSDA is the reason for the erroneous magnetic solution.

Local-density approximation $+ U$ (LDA $+ U$) is a simple method within the framework of DFT going beyond LSDA by treating exchange and correlation differently but only for a chosen set of states, which in the case of FeAl comprises the $3d$ orbitals of iron. The density functional in the framework of LDA $+ U$ can be written as

$$F^{\mathrm{LDA}+U}[\rho, m_\sigma, \hat{n}] = F^{\mathrm{LSDA}}[\rho, m_\sigma]$$
$$+ E^{ee}(\hat{n}) - F^{\mathrm{dc}}(\hat{n}), \quad (1)$$

where ρ and m_σ are the electron and magnetization density, respectively. $\hat{n}$ is the occupation number matrix and E^{ee} is the intra-atomic electron-electron interaction among the $3d$ orbitals of Fe in accordance with a multiband Hubbard model [11,12]. The "double-counting" term F^{dc} is an approximation to the electron-electron interaction (for the $3d$ orbitals) contained already in F^{LSDA}. In the original scheme [11] F^{dc} was chosen such that $F^{\mathrm{LSDA}+U}$ reduces to F^{LSDA} when the orbitals are equally occupied. This scheme complies with the density functional theory and we call it LDA $+ U^{\mathrm{DFT}}$. In a later version [13] the double-counting term was taken to satisfy an atomiclike limit of LSDA, which allows us to approximately remove the electron self-interaction; hence we call it LDA $+ U^{\mathrm{SIC}}$. The difference between the two versions can clearly be seen if the population number matrix is diagonal and only the Hartree term is considered. The potentials $V_{m,\sigma}^{\mathrm{DFT}}$ and $V_{m,\sigma}^{\mathrm{SIC}}$ which are added to the LSDA potential for the orbital m are then

$$V_{m,\sigma}^{\mathrm{DFT}} = U(\langle n_\sigma \rangle - n_{m,\sigma}); \qquad V_{m,\sigma}^{\mathrm{SIC}} = U(\tfrac{1}{2} - n_{m,\sigma}),$$
$$(2)$$

where $\langle n_\sigma \rangle$ is the average number of electrons in the $3d$ orbitals of Fe with spin σ and $n_{m\sigma}$ is the corresponding occupation of the mth orbital.

LDA $+ U^{\mathrm{SIC}}$ is based on spherical atom results so that its application in full potential methods it is not well defined. The above potentials are included only inside the atomic spheres and thus the factor $1/2$ in $V_{m,\sigma}^{\mathrm{SIC}}$ is correct only for an isolated atom whereas in a solid it should be scaled down, since only part of the orbital is contained inside the atomic sphere. Both LDA $+ U$ versions were compared in a recent paper [14]. In the present work we also apply both methods as discussed below.

To calculate the electronic and magnetic structure of FeAl we employed the FP-LAPW method as embodied in the WIEN97 code [5]. All calculations presented were done for the experimental lattice constant (5.496 bohrs). The im-

plementation of LDA $+ U$ in the FP-LAPW code follows the rotationally invariant scheme described by Liechtenstein et al. [15]. The wave function in the atomic region was expanded up to $l = 10$, and the plane-wave cutoff was chosen to be $R_{MT}K_{\max} = 8$ which amounts to about 160 plane waves (depending on $\mathbf{k}$). The nonspherical part of the potential was expanded into spherical harmonics up to $l = 6$. To provide a reliable Brillouin zone integration, a set of 165 $\mathbf{k}$-points in the irreducible wedge of the Brillouin zone was used. For the LSDA part the interpolation formula given by Perdew and Wang [16] was used. In our LDA $+ U$ calculations the U value applied to the Fe-d orbitals has been treated as an external parameter. The second parameter J, the exchange integral, appearing in the LDA $+ U$ formalism [17] was set to the usual Fe value of 0.95 eV and kept fixed. It has been tested that a variation of J has only a minor effect on the electronic structure.

Figure 1 shows the DOS of non-spin-polarized calculations with $U = 0$ and $U = 5$ eV within the LDA $+ U^{\mathrm{DFT}}$ scheme. For $U = 0$ (lower panel in Fig. 1) the resulting
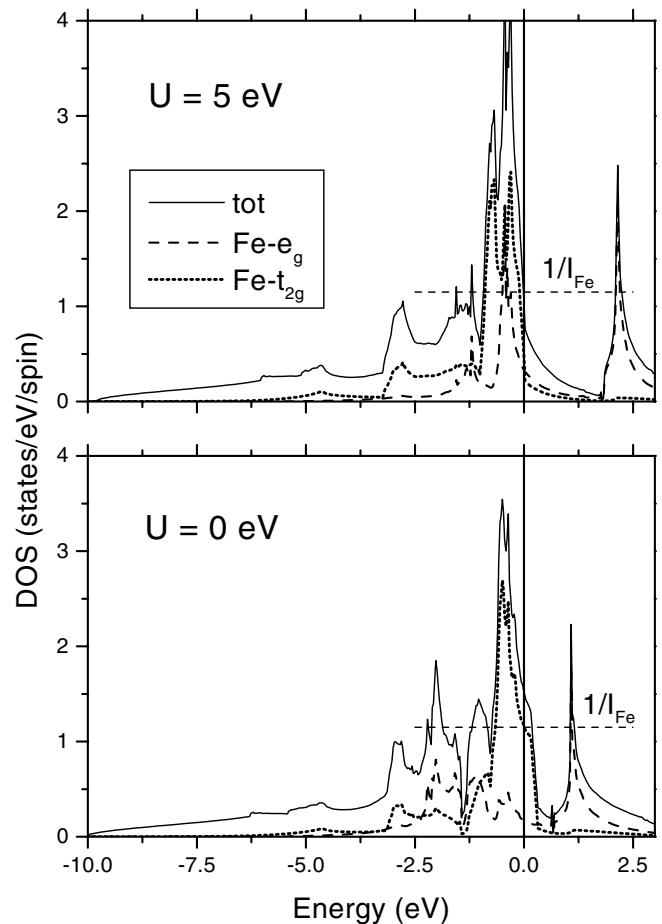

FIG. 1. Density of states (DOS) for $U = 5$ eV (upper panel) and $U = 0$ eV (lower panel) for FeAl and the decomposition into the Fe-e_g and Fe-t_{2g} manifolds for an LDA $+ U^{\mathrm{DFT}}$ calculation in the nonmagnetic state. The horizontal dashed line marks the critical value for the DOS at ε_F above which the Stoner criterion ($1/I_{\mathrm{Fe}}$) would be fulfilled.

electronic structure is equivalent to a bare LDA calculation and resembles the situation described earlier [3]. The Fermi energy ε_F lies right in a peak of the Fe d-DOS, which is large enough to fulfill the Stoner criterion. The Fe d-DOS is decomposed into the two symmetry components, namely, the e_g states, which mainly describe the Fe-Fe interaction, and the t_{2g} states, which form a "nonbonding" state just below ε_F and which are entangled in the Fe-Al interaction at energies between -3 and -1 eV. The upper panel in Fig. 1 shows the DOS as calculated from LDA + U^{DFT} for $U = 5$ eV. The stronger electron correlation leads to changes in the DOS which can be attributed to a redistribution of the respective spectral weights. The main effect is a lowering of the t_{2g} with respect to the e_g states. As a consequence the energy difference between the Fe-t_{2g} and Al-p states becomes smaller, which results in an increased overlap. Simultaneously ε_F is pushed towards the "gap" between the occupied Fe-t_{2g} and the unoccupied Fe-e_g states so that the DOS at ε_F becomes smaller and too low for the Stoner criterion to be fulfilled. This happens for $U \sim 3.7$ eV where the DOS at ε_F drops below the critical value of 1.15 states/spin/eV. Thus a nonmagnetic state is found for both the LDA + U^{DFT} and the LDA + $\mathrm{U^{SIC}}$. Although, at first sight, $U \geq 3.7$ eV seems to be large for a metallic system, the resulting energy shifts are small as can be seen from Fig. 1. This happens due to the strong screening of U by the conduction electrons. It is known that rather large U values in an all electron treatment are equivalent to much smaller U values in a d-band only tight-binding model.

To our knowledge FeAl is the first case in which the application of LDA + U leads to a *nonmagnetic ground state* when LDA gives a *magnetic ground state,* whereas it is the other way around in cases studied so far.

Figure 2 shows the difference in the total energy between the nonmagnetic (by constraining $M = 0$) and the ferromagnetic case $\Delta E = E_{nm} - E_{fm}$ and the respective Fe magnetic moments as a function of U with the fixed value of J given above. As a general feature for $U = 0$ a ferromagnetic ground state is obtained and the nonmagnetic state is unstable. Upon increasing U the ferromagnetic state turns metastable and the nonmagnetic state $M = 0$ becomes the stable solution. For the LDA + U^{DFT} scheme (lower panel) with $U \geq 3.7$ eV the nonmagnetic solution becomes the stable one. For $U \simeq 5$ eV the metastable ferromagnetic solution disappears completely; only a nonmagnetic ground state exists. Increasing U further again leads to a ferromagnetic solution which is lower in energy and exhibits a slightly larger magnetic moment than in the low U range.

Applying the LDA + U^{SIC} scheme (upper panel) yields very similar results in the low U range also giving a nonmagnetic solution for $U \geq 4$ eV. However, starting at about $U \geq 3$ eV an additional high moment state with a magnetic moment $> 2\mu_B$ appears. The respective total
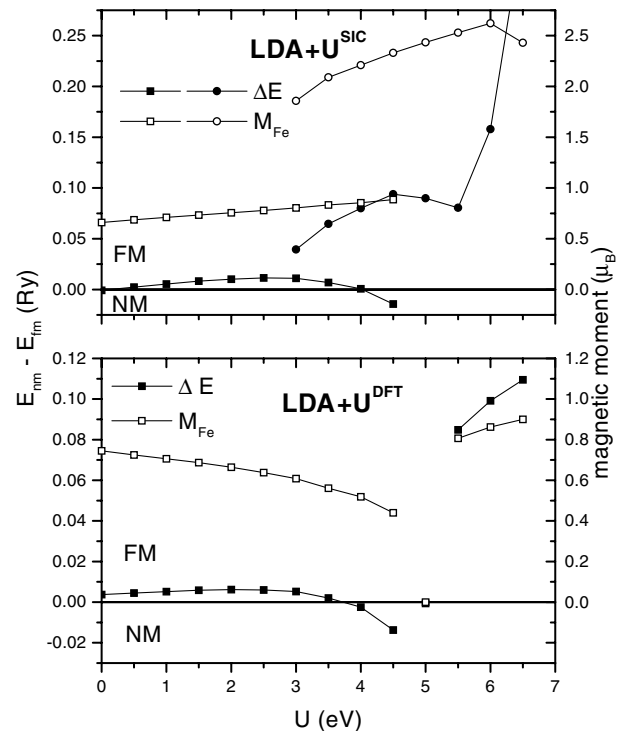

FIG. 2. Difference in the total energies between the nonmagnetic and the ferromagnetic state and the magnetic moment as a function of U. Lower panel: results for the LDA + U^{DFT} scheme; upper panel: results for the LDA + U^{SIC} scheme. Full symbols denote ΔE; open symbols denote the magnetic moment. For LDA + U^{SIC} (upper panel) a low-moment (squares) and a high-moment (spheres) state exist.

energy of this state is below the nonmagnetic solution and drops sharply for $U \geq 5.5$ eV. The simultaneous existence of two total energy minima is a well known property of some materials, such as fcc Fe, and has been studied extensively earlier [18]. No such feature could be found for the LDA + U^{DFT} scheme.

Within the current understanding of the LDA + U scheme a magnetic solution will appear for large values of U. The striking discrepancy between the two schemes in the range for $U > 4$ eV raises the question about the physical relevance of these high moment states which could be an artifact in the large U limit.

The fact that U acts differently on the Fe-e_g and Fe-t_{2g} manifolds is reflected in the magnetic moments. In both LDA + U schemes the magnetic moment comes predominantly from the t_{2g} electrons for small values of U. For large U, however, LDA + U^{SIC} and LDA + U^{DFT} show a different behavior. In the latter case the moment changes abruptly to e_g character. For LDA + U^{SIC} the magnetic moment in the high-moment state at first is about equally composed of e_g and t_{2g} contributions but for $U \gtrsim 5$ eV it originates mainly from the t_{2g} electrons. This completely different behavior in the large U regime is also the reason for the observed strong variation in the $\Delta E(U)$ behavior found for LDA + U^{SIC} and LDA + U^{DFT} and

comes from the different treatment described by Eq. (2). For V^{DFT} the deviation from the average occupation number is essential, whereas for V^{SIC} the deviation from half filling is the key quantity.

Apart from describing a nonmagnetic ground state for finite values of U by LDA $+ U^{DFT}$, our results pose the following question: Why should an ordinary metallic alloy such as FeAl be ill described by conventional LDA schemes which work so successfully for a large number of similar metallic systems? The answer is most probably buried in the peculiar electronic structure of this compound. The crystal field splitting almost completely separates the Fe-d states into their e_g and t_{2g} components. The e_g electrons form weak σ bonds between neighboring Fe atoms but over a relatively large distance of one lattice constant. Consequently the resulting bands are flat and almost atomiclike. Parts of the t_{2g} electrons are involved in the interaction with the Al-p states. Because of the energetic difference between the Al-p and the Fe-t_{2g} states this interaction is also weak. Again the band dispersion is small and atomiclike states are found. It is this atomiclike character of the narrow Fe d-bands which requires an improved correlation treatment as provided by the LDA $+ U$ scheme. However, the fact which makes FeAl so different from the usual LDA $+ U$ applications is that for small values of U the Fe-Al interaction increases which leads to a broadening of the respective bands until a nonmagnetic ground state is formed. The effect of U is of the same order of magnitude as the crystal field splitting according to e_g and t_{2g}. Only for large U values magnetism comes back in agreement with the physical expectation. It should be pointed out that the reason for this result is not stronger correlation but rather a different, and presumably better, treatment of correlation which causes the disappearance of magnetism.

In conclusion, we have found that for FeAl an initially incorrectly predicted magnetic ground state by standard LSDA calculations disappears upon applying the LDA $+ U$ potential. Within the LDA $+ U$ scheme we found a range of U values for which a stable nonmagnetic solution exists in agreement with experiment. This result is highly unusual since the introduction of strong atomiclike electron correlation normally favors the formation of magnetic order.

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