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Electronic correlations, magnetism, and structure of Fe-Al subsystems: An LDA+U study

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The influence of electronic correlations on the intimate relations between magnetism and structure of Fe-Al subsystems is investigated by the LDA+U method in the two currently used versions, around mean field (AMF) and fully localized limit (FLL). The calculations were performed with the new Stuttgart spin-polarized *ab initio* mixed-basis pseudopotential LDA+U code which is able to calculate both total energies and forces and thus to deal with structural relaxations. Both LDA+U versions yield coherent results concerning the energetical hierarchy for Fe_3Al, i.e., a stabilization of the experimentally stable $D0_3$ structure against the $L1_2$ structure at moderate values of *U*, although the details concerning absolute energy shifts, lattice constant, and magnetism differ. For Fe impurities in Al the AMF result resembles the local-spin-density approximation result of a vanishing magnetic moment through structural relaxations, whereas with the FLL functional the magnetic moment remains finite.

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I. INTRODUCTION

Former experimental and theoretical investigations revealed that there is a very delicate interplay between magnetism and structural stability in the alloy system Fe-Al. We mention just three examples. First, the magnetic state of a substitutional Fe impurity in a fcc-Al host has been calculated within the framework of the *ab initio* density-functional theory in local-spin-density approximation (LSDA). Working at the theoretical LSDA lattice constant of Al (which is about 1% smaller than the experimental lattice constant) a magnetic Fe impurity was found if the local atomic relaxations of the Al atoms around the impurity atom were neglected. When allowing for a full structural relaxation which leads to a shift of the nearest-neighbor atoms of about 4% of the interatomic distance towards the impurity site, the local moment vanishes.[1] However, when working at the experimental lattice constant, then unreasonably large local atomic relaxations would be necessary to destroy the magnetic moment.[2] Hence, spin fluctuations accompanied with a high Kondo temperature are still not totally unreasonable for this impurity problem, although experiments using different techniques did not find evidence of magnetic behavior of Fe impurities in Al (see references given in Ref. 2). Second, for the ordered compound B2-FeAl the situation is even more complicated (see Ref. 3 and references therein). There is experimental evidence that perfectly ordered FeAl exactly at the stoichiometric composition (which is very hard to prepare experimentally) does not exhibit a macroscopic magnetic moment, whereas LSDA calculations yield a ferromagnetic ground state when allowing for a collinear spin polarization of the atoms. To investigate the influence of electronic correlations beyond LSDA, calculations within the framework of the LDA+U method[4,5] were performed at the experimental lattice constant. A breakdown of the ferromagnetic moment was found for a small range of rather large *U* values.[6] However, in agreement with Ref. 7 we found by our own LDA+U calculations performed in the context of the present work that the magnetic moment survives even for these *U* values if a volume relaxation to the theoretical lattice constant of the LDA+U calculation is performed. Such volume effects are essential, as an Fe antistructure atom in B2-FeAl carries a large magnetic moment, and it was suggested in Ref. 8 that therefore there might be a very large relaxation volume of the Fe antistructure atom. Third, for Fe_3Al LSDA calculations yield[9] a ferromagnetic $D0_3$ ground-state structure [Fig. 1(a)] in agreement with the experiments, but a calculation with the generalized-gradient approximation (GGA) after Perdew, Burke, and Ernzerhof[10] (PBE) slightly preferred a ferromagnetic $L1_2$ ground state [Fig. 1(b)]. This failure was attributed to an overestimation of the magnetic energy in GGA-PBE. Additionally, also in the LSDA comparison[9] these two competing structures are nearly energetically degenerate at the experimental equilibrium volume of $D0_3$-Fe_3Al. Altogether, in all three considered Fe-Al sub-

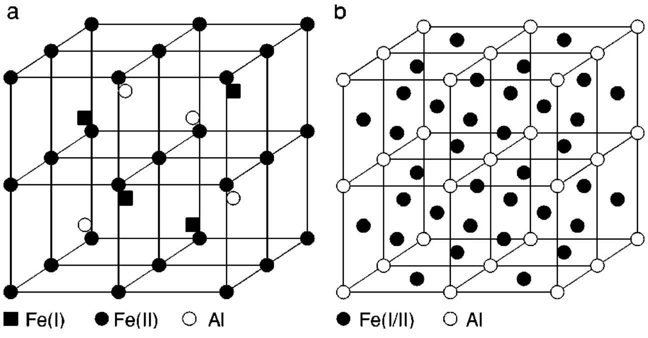

FIG. 1. (a) $D0_3$-Fe_3Al structure and (b) $L1_2$-Fe_3Al structure.

systems (Fe impurity in Al, B2-FeAl, Fe_3Al) there is an intimate interplay between structure and magnetism.

Former calculations within the framework of the LSDA have shown[11] that the systematics of the formation of magnetic moments on Fe atoms in various transition-metal hosts depends very sensitively on the structure (especially on the symmetry) of the transition-metal hosts. We now concentrate on the additional influence of electronic correlations beyond LSDA.

The system Fe-Al is a mixture of the main-group element Al which contributes delocalized and weakly correlated *s* and *p* electrons and the $3d$ transition-metal atom Fe which exhibits in addition rather strongly localized and thus rather strongly correlated $3d$ electrons. It is likely that this mixture between weakly and strongly correlated states also contributes to the intimate relation between magnetism and structure. In the present paper we therefore investigate the influence of on-site correlations on the Fe atoms by the LDA$+$U method. Because for B2-FeAl LDA$+$U calculations have been already performed (comments, including our own results, were given above) we report only on our calculations for Fe_3Al and for Fe impurities in Al. For the latter subsystem we describe also the results of our GGA calculations, because there are no such calculations so far.

The LDA$+$U method has been introduced originally for the description of systems with very strong electronic correlations such as some transition-metal oxides. Our guess is that it yields at least the correct trends when being applied to moderately correlated $3d$ transition metals and their compounds, but quantitative results may be less reliable. In general, the LDA$+$U method can be understood as the ideal method in the limit of very strong electronic correlations for insulating, long-range ordered systems. In contrast, the L(S)DA should become definitively reliable for metallic systems in the limit of very weak electronic correlations. In the limit of very small U the LDA$+$U method tends to the LSDA, and therefore for moderately correlated systems with small U the application of both schemes to such systems can be justified in similar ways. In the LDA$+$U method the on-site correlations are described in the framework of a mean-field approach, but the effect of quantum fluctuations is neglected. Note, however, that these fluctuations may be important. It has been argued by Petukhov *et al.*[12] that for B2-FeAl the effect of quantum fluctuations may be more important than the mean-field effect of the correlations. Furthermore, for the Heusler compound $L2_1$-Fe_2VAl which is obtained from $D0_3$-Fe_3Al when replacing the Fe(I) atom by V a strongly enhanced effective electronic mass has been observed[13] which may arise from spin fluctuations. This may be considered as a further hint for essential quantum fluctuations also in Fe_3Al. Therefore, much more work is necessary to decide whether the mean-field effect of the on-site correlations or the correlated dynamical fluctuations are more important in the Fe-Al system.

II. THEORETICAL APPROACH

In the LDA$+$U method the electronic system is separated in a localized and a itinerant subsystem.[15] In the scope of this paper, the localized subsystem will be identified with the $3d$ orbitals of the Fe atoms. The energy expression for the whole electronic system in LDA$+$U reads as[5,16]

$$E_{LDA+U}[\{\rho^s\},n]=T_s[\{\rho^s\}]+\int_{\Omega_c}d^3r v_{ext}(\mathbf{r})\rho(\mathbf{r}) +E_H[\{\rho^s\}]+E_{xc}^{LSDA}[\{\rho^s\}]+E_{ee}^{loc}[n] -E_{dc}[n], \tag{1}$$

where $\rho^s(\mathbf{r})(s\underline{=}\uparrow,\downarrow)$ are the total electron spin densities with $\rho=\rho^s+\rho^s$, T_s is the kinetic energy for noninteracting electrons, Ω_c is the volume of the unit cell, v_{ext} is the external potential, E_H is the Hartree energy, and E_{xc}^{LSDA} is the exchange-correlation energy in LSDA. The explicit new contributions in the LDA$+$U method are the quantities E_{ee}^{loc}, the electron-electron interaction energy of the localized subsystem, and E_{dc}, a double-counting correction energy which shall account for the energy contributions included both in E_{ee}^{loc} and the remaining terms. The quantity n describes the orbital density matrix of the localized subsystem. The elements of this matrix are given by $n_{mm'}^{\alpha s}$, where α denotes the atom in the unit cell and m,m' are magnetic quantum numbers of the d states. According to a mean-field approximation of the multiband Hubbard model, a representation of $E_{ee}^{loc}[n]$ can be written as[5]

$$E_{ee}^{loc}=\frac{1}{2}\sum_{\alpha\{m\}ss'}n_{m_1m_2}^{\alpha s}(U_{m_1m_3m_2m_4}-\delta_{ss'}U_{m_1m_3m_4m_2})n_{m_3m_4}^{\alpha s'}. \tag{2}$$

The on-site Coulomb matrix elements in Eq. (2) can be evaluated as a linear combination of effective Slater integrals F_k:

$$U_{m_1m_3m_2m_4}=\sum_k a_k(m_1,m_2,m_3,m_4)F_k, \tag{3}$$

where the a_k are the Gaunt coefficients[5] expressed via spherical or cubic harmonics. For d states only the integrals F_0, F_2, and F_4 contribute to the sum in Eq. (3). Via certain sum rules[14] one can relate the Coulomb matrix elements (3) to averaged values U and J and thereby, in the case of d electrons $(l=2)$, obtain the following identification:

$$U=F_0,\quad J=(F_2+F_4)/14. \tag{4}$$

For a complete mapping from effective Slater integrals to generalized Hubbard parameters one still needs a further relation. This is given by the ratio F_4/F_2 which is constant to a good accuracy for $3d$ elements with a value of 0.625 (see Ref. 5 and references therein). The double-counting term E_{dc} is a crucial part[12] of the LDA$+$U method. In the so-called around mean field (AMF) version[4,14] of LDA$+$U this term takes the following form:

$$E_{dc}^{AMF}=\sum_{\alpha}\left\{Un^{\alpha s}n^{\alpha\bar{s}}+\frac{l(U-J)}{2l+1}\sum_{s}(n^{\alpha s})^2\right\}$$
$$=\frac{U}{2}\sum_{\alpha}(n^{\alpha})^2-\frac{U+2lJ}{2(2l+1)}\sum_{\alpha s}(n^{\alpha s})^2, \qquad (5)$$

whereas in the so-called fully localized limit (FLL) version[15,14,17] it is written as

$$E_{dc}^{FLL}=\frac{U}{2}\sum_{\alpha}n^{\alpha}(n^{\alpha}-1)-\frac{J}{2}\sum_{\alpha s}n^{\alpha s}(n^{\alpha s}-1). \qquad (6)$$

In the AMF version of LDA+U, E_{dc} is constructed in such a way that the local electron-electron interaction is only taken into account when the occupation of the localized states deviates from the overall average occupation.[4] In contrast, in the FLL version it is expected that the full energy of the uncoupled localized subsystem for a given integer number of electrons in this subsystem is satisfyingly described within LSDA. In the latter mainly the variation of this energy with respect to the number of electrons is not properly described,[18] i.e., the well-known discontinuity in the exchange-correlation potential is missing. Hence, this full energy, expressed by the generalized Hubbard parameters, is identified as E_{dc}. Therewith one can regain the jump in the potential when going through integer occupations of the orbitals,[17,18] as dictated by the exact exchange-correlation potential. With this feature, the FLL version is well designed for the limit of strong correlations.[12]

For the complete explicit orbital potential in LDA+U one gets by deriving the new corresponding Kohn-Sham equations (see, e.g., Ref. 16) the following expressions for the two representations:

$$v_{m_1m_2}^{\alpha s,AMF}=\sum_{m_3m_4s'}(U_{m_1m_3m_2m_4}-\delta_{ss'}U_{m_1m_3m_4m_2})n_{m_3m_4}^{\alpha s'}$$
$$-\delta_{m_1m_2}Un^{\alpha}+\delta_{m_1m_2}\frac{U+2lJ}{2l+1}n^{\alpha s}, \qquad (7)$$

$$v_{m_1m_2}^{\alpha s,FLL}=\sum_{m_3m_4s'}(U_{m_1m_3m_2m_4}-\delta_{ss'}U_{m_1m_3m_4m_2})n_{m_3m_4}^{\alpha s'}$$
$$-\delta_{m_1m_2}U\left(n^{\alpha}-\frac{1}{2}\right)+\delta_{m_1m_2}J\left(n^{\alpha s}-\frac{1}{2}\right), \qquad (8)$$

with $n^{\alpha s}=\Sigma_m n_{mm}^{\alpha s}$ and $n^{\alpha}=\Sigma_s n^{\alpha s}$.

When expressing Eqs. (2), (5), and (6) through Eqs. (7) and (8), inserting the result in Eq. (1), and eliminating, as usual,[19] T_s via the integrated Kohn-Sham equations, the variational energy expression[19] for the electronic system in the LDA+U method is given by

$$E_{LDA+U}=\sum_{i}^{occ}\epsilon_i+\int_{\Omega_c}d^3r\rho(\mathbf{r})\left(\frac{1}{2}v_H(\mathbf{r})+\varepsilon_{xc}(\rho^s,\rho^{\bar{s}},\mathbf{r})\right)$$
$$-\int_{\Omega_c}d^3r\left(\sum_{s}\rho^s(\mathbf{r})v_{xc}^{s,in}(\mathbf{r})+\rho(\mathbf{r})v_H^{in}(\mathbf{r})\right)+E_U. \qquad (9)$$

Here ϵ_i is an eigenvalue of the Kohn-Sham particles, v_H is the Hartree potential, ε_{xc} the exchange-correlation energy per particle of the uniform electron gas, and v_{xc}^s the exchange-correlation potential in LSDA. The energy term E_U is written for the two versions of the LDA+U method as

$$E_U^{AMF}=\frac{1}{2}\sum_{\alpha m_1m_2s}v_{m_1m_2}^{\alpha s,AMF}n_{m_1m_2}^{\alpha s}-\sum_{\alpha m_1m_2s}v_{m_1m_2}^{\alpha s,AMF,in}n_{m_1m_2}^{\alpha s}, \qquad (10)$$

$$E_U^{FLL}=\frac{1}{2}\sum_{\alpha m_1m_2s}v_{m_1m_2}^{\alpha s,FLL}n_{m_1m_2}^{\alpha s}+\frac{U-J}{4}\sum_{\alpha}n^{\alpha}$$
$$-\sum_{\alpha m_1m_2s}v_{m_1m_2}^{\alpha s,FLL,in}n_{m_1m_2}^{\alpha s}. \qquad (11)$$

The superscript ''in'' in the Eqs. (9)–(11) specifies the corresponding potentials as input potentials in the respective Kohn-Sham cycle after which the total energy is calculated. These input potentials, together with the eigenvalue sum, stem from the elimination of T_s. In the case of self-consistency, of course, this additional superscript vanishes. We have implemented the LDA+U method in both the AMF and the FLL versions into our *ab initio* mixed-basis pseudopotential[20] (MBPP) code. The orbital density matrix thereby is computed by projecting the crystal pseudovalence functions $\psi_{\mathbf{k}b}^s$ onto cubic harmonics centered at the site α. In $\psi_{\mathbf{k}b}^s$ $\mathbf{k}$ is a Bloch vector and b the band index. By using the time-reversal symmetry applied to the $\psi_{\mathbf{k}b}^s$ one can easily show that the orbital density matrix n is always real in this case.

In the MBPP code the basis set consists of plane waves and a few additional localized functions per atom. The latter allow for a smaller cutoff energy $E_{cut,pw}$ for the plane waves when treating, for instance, transition-metal compounds. Because these localized functions are nonoverlapping, it is possible to calculate in addition very elegantly the forces including the incomplete-basis-set corrections, following essentially the general procedure[21] applied to the derivation of MBPP-L(S)DA forces.[22] An essential point thereby is that the derivative of the orbital density matrix drops out (a numerical evaluation of this derivative would be terribly complicated). Therefore our LDA+U code is able to calculate both total energies and forces.

For the LSDA part of the LDA+U functional we used the LSDA exchange-correlation functional of Perdew and Wang.[23] Nonzero values of U and J are attached to those atoms with strong on-site correlations. Accordingly, we chose $U=J=0$ for the Al atoms with the itinerant s and p states. For the Fe atoms the d states are more localized, especially for the Fe(I) atoms in the $D0_3$ structure. This be-

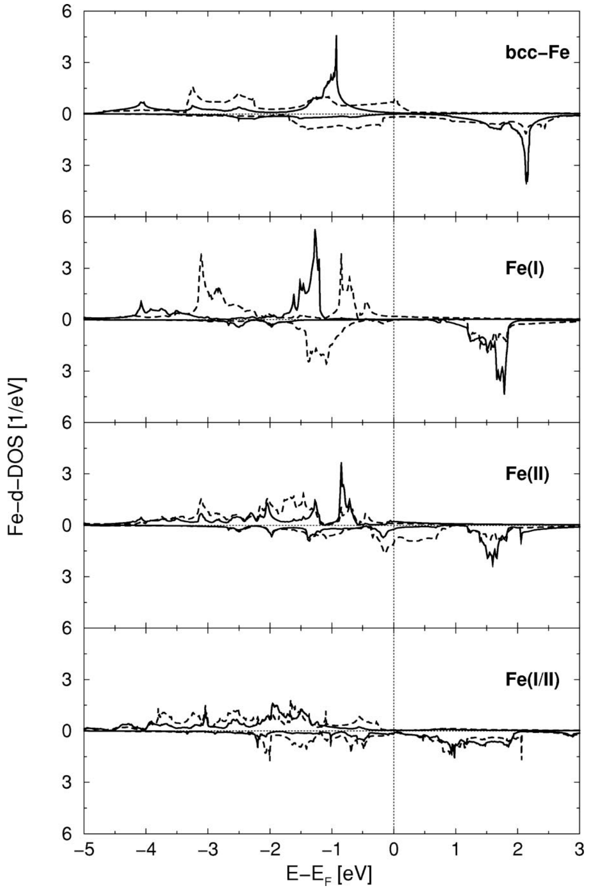

FIG. 2. The local density of states for the t_{2g} states (broken lines) and the e_g states (full lines) of Fe atoms in various crystal environments.

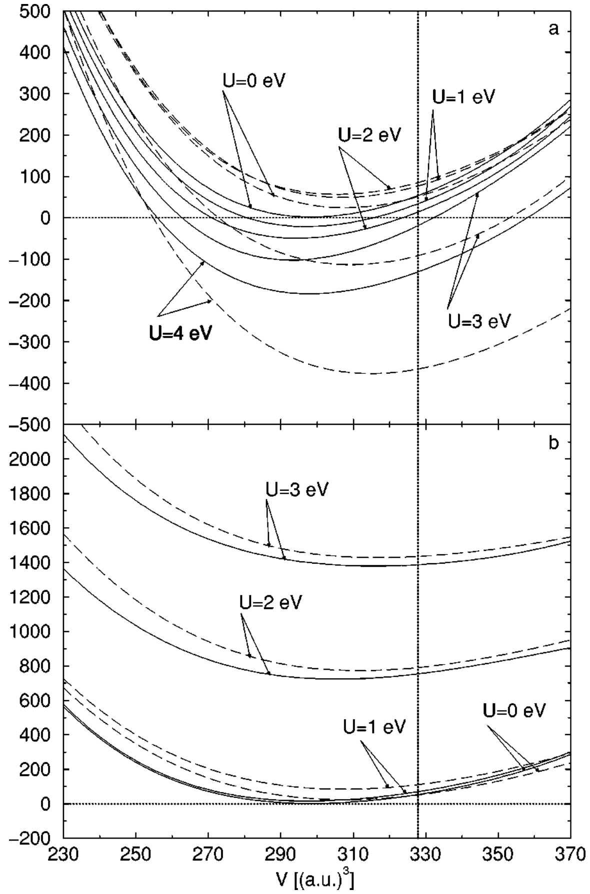

FIG. 3. Total energy as a function of the volume of the elementary unit cell for D0$_3$-Fe$_3$Al (solid lines) and L1$_2$-Fe$_3$Al (broken lines) according to the AMF (a) and the FLL (b) versions of the LDA+U method. The dotted vertical line marks the experimental lattice constant.

comes obvious from the GGA local *d* density of states plots shown in Fig. 2. It is expected that the crystal-field splitting of the *d* states into t_{2g} and e_g states is strong for the case of substantial localization, and the figure therefore gives a hint that the *d* states of the Fe(I) atoms of the D0$_3$ structure are more localized than the *d* states for the Fe(II) atoms, for the pure bcc-Fe atoms, and for the crystallographically equivalent Fe(I/II) atoms in the L1$_2$ structure. Therefore it may well be that LSDA and GGA which are designed for more itinerant systems are inadequate in principle to describe this mixture of localized and itinerant *d* states in D0$_3$-Fe$_3$Al, and this calls for an investigation by the LDA+U method with nonzero *U* and *J* for the Fe atoms. For the calculations discussed below we used the same values for *U* and *J* (*J* fixed to[6] 0.95 eV), respectively, for the Fe atoms in all considered systems. In addition, we have performed calculations for the D0$_3$ structure where we attached nonzero *U* and *J* only to the Fe(I) sites. This had no qualitative influence on the question whether the D0$_3$ state or the L1$_2$ state of Fe$_3$Al is more stable, but affected the magnetic moments (see Sec. III).

An additional parameter in the LDA+U calculation is the radius $r^{Fe}_{cut,U}$ for the extension of the localized *d* states to which the Hubbard parameters are attached. In the calculations, we chose the radius $r^{Fe}_{cut,U}$ as the radius for which in a MBPP-LSDA calculation these *d* states are occupied by the atomic value of six electrons. Therewith we obtained $r^{Fe,D0_3}_{cut,U}=2.20$ a.u. for Fe(I) and Fe(II) in the D0$_3$ structure and $r^{Fe,L1_2}_{cut,U}=2.25$ a.u. for Fe(I/II) in the L1$_2$ structure. By using $r^{Fe,L1_2}_{cut,U}=2.20$ a.u. also for the latter, only marginal quantitative differences in the total energy and the magnetic moment resulted. For the Fe impurity in fcc-Al we used the value $r^{Fe,imp}_{cut,U}=2.10$ a.u.

In the MBPP calculations for Fe$_3$Al 110 *k* points for the D0$_3$ and 120 *k* points for the L1$_2$ structure were used in the irreducible part of the first Brillouin Zone (BZ). A cutoff energy of $E_{cut,pw}=24$ Ry was employed for both structures.

For the treatment of an Fe impurity in fcc-Al, a supercell of 107 Al atoms with one Fe atom in the center was introduced. For all corresponding MBPP calculations 10 *k* points in the irreducible part of the first BZ were used. The value of $E_{cut,pw}$ for these calculations was set to 16 Ry. Throughout all the MBPP calculations a Gaussian smearing of 0.05 eV was used.

III. RESULTS AND DISCUSSION FOR Fe$_3$Al

Figure 3 shows for the D0$_3$ structure (solid lines) and the L1$_2$ structure (broken lines) the total energies [referred to the respective total energy $E_{LSDA}(\mathrm{D0}_3)$] as a function of the volume of the unit cell for various values of U, both for the AMF (top) and for the FLL (bottom) versions of the LDA +U method. For $U<3$ eV in both versions the total magnetic moment drops by about $2\mu_\mathrm{B}$ for the $\mathrm{D0}_3$ structure and about $1\mu_\mathrm{B}$ for the $\mathrm{L1}_2$ structure at Ω_c around 290 (a.u.)^3, when coming from higher volumes. Still, for these U values all the binding curves are smooth over the inspected volume range. The important effect of these moderate values of U is the consolidated stabilization of the $\mathrm{D0}_3$ over the $\mathrm{L1}_2$ structure over the whole volume range. It should be recalled that experimentally also a $\mathrm{D0}_3$ ground state is found whereas GGA-PBE calculations[9] yield a $\mathrm{L1}_2$ ground state. Furthermore, although LSDA calculations reveal the correct energetical hierarchy according to experiment for the theoretical equilibrium volume, this hierarchy (as already mentioned in the Introduction) switches right at the experimental equilibrium volume in these calculations.[9] For $U\geqslant 3$ eV the situation changes for the AMF version. There, a low-spin phase becomes stable over the whole volume range for both competing structures. In addition to the stable lower magnetic moment, the $\mathrm{L1}_2$ structure is favored over the $\mathrm{D0}_3$ structure for $U\geqslant 3$ eV in this LDA+U method. In all cases, only the binding curve corresponding to the stable phase for each structure is depicted in Fig. 3. For the FLL version, no such low-spin phases appear in the calculations. The $\mathrm{D0}_3$ structure remains stable using this version also for $U\geqslant 3$ eV.

In Fig. 3 one can also see qualitative differences in the predicted theoretical equilibrium volumes for $\mathrm{Fe}_3\mathrm{Al}$ with increasing U between both schemes of the LDA+U method. Interestingly, whereas in FLL the equilibrium volume of $\mathrm{D0}_3$-$\mathrm{Fe}_3\mathrm{Al}$ for moderate values of U increases towards the experimental value, in AMF the notoriously underestimated LSDA value is even further lowered in this regime. This is surprising, as in our test calculations for the strongly correlated NiO both LDA+U versions showed an increase of the equilibrium volume from the LSDA to the experimental value.

Figure 4 shows for the $\mathrm{D0}_3$ and the $\mathrm{L1}_2$ structures the magnetic moments at the experimental lattice constant of $\mathrm{D0}_3$-$\mathrm{Fe}_3\mathrm{Al}$ as a function of U. Experimentally, the local magnetic moments from neutron-diffraction measurements[24] are $M_{Fe(I)}=2.18\mu_\mathrm{B}$ and $M_{Fe(II)}=1.50\mu_\mathrm{B}$. For the AMF version we observe a transition to the low-spin state with increasing U. For the $\mathrm{D0}_3$ structure this transition is accompanied by a collapse of the Fe(II) moment. It should be noted that this collapse and hence the transition to the low-spin state takes place at a much higher value of U around 6 eV, when we chose $U=J=0$ for the Fe(II) atoms (see Sec. II). However, this had no influence on the qualitative behavior of the energy difference $E(\mathrm{D0}_3)-E(\mathrm{L1}_2)$ as a function of U. For the FLL version there is no collapse of the Fe(II) moments for the considered values of U and hence no transition to a low-spin state. Whereas in the AMF version the magnetic Fe moments tend to decrease with increasing U, in the FLL version they increase slightly. By choosing $U=J=0$ for the Fe(II) atoms, the magnetic moments of these Fe atoms, as expected, remain rather constant when increasing U for the Fe(I) atoms. Although in this scheme the qualitative character of energetic differences between the $\mathrm{D0}_3$ and the $\mathrm{L1}_2$ structures is the same, the stabilization of $\mathrm{D0}_3$ is even more pronounced.

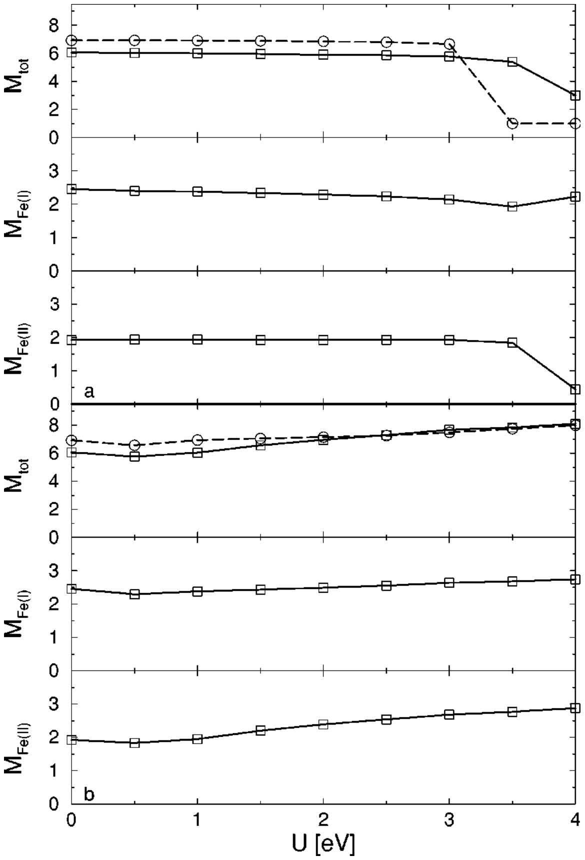

FIG. 4. The magnetic moments at the experimental lattice constant for $\mathrm{D0}_3$-$\mathrm{Fe}_3\mathrm{Al}$ (solid lines) and $\mathrm{L1}_2$-$\mathrm{Fe}_3\mathrm{Al}$ (broken lines) according to the AMF (a) and FLL (b) versions of the LDA+U method. All moments in μ_B.

To summarize, for moderate U both the AMF and the FLL versions of LDA+U stabilize the correct $\mathrm{D0}_3$ structure for $\mathrm{Fe}_3\mathrm{Al}$, but they sometimes yield considerably different results for the equilibrium volume and the magnetic moments.

IV. RESULTS AND DISCUSSION FOR THE FE IMPURITIES IN AL

To study the behavior of substitutional Fe impurities in fcc-Al we constructed supercells containing 107 Al atoms and one central Fe atom, and we repeated these supercells periodically for our LSDA,[23] GGA,[10] and LDA+U calculations. In those supercells, a maximum of ninth nearest-neighbor distance between the atoms is included. The LSDA and GGA data correspond to the respective theoretical lattice constants of fcc-Al obtained by these methods (7.519 a.u. and 7.626 a.u.). In contrast, the LDA+U calculations were performed for the LSDA equilibrium lattice constant (the experimental lattice constant of fcc-Al is 7.65 a.u.) and a value of $U=2$ eV was inserted to investigate the influence of a moderate U value to the problem.

TABLE I. Magnetic moments, energy gain $E^{relax}=E^{relax}_{tot}-E^{unrelax}_{tot}$, and structural relaxations. The relaxations are given up to the sixth nearest-neighbor distance of the supercell which ranges to ninth nearest-neighbor distances. Positive relaxation values denote shifts of the atomic positions towards the Fe atom, and negative values belong to shifts away from the Fe atom.

	LSDA PW-92	GGA PBE	LDA+U AMF, $U=2$ eV	LDA+U FLL, $U=2$ eV
a (a.u.)	7.519	7.626	7.519	7.519
$M^{unrelax}_{tot}$ (μ_B)	1.62	2.09	1.60	2.15
$M^{unrelax}_{Fe}$ (μ_B)	1.63	2.18	1.63	2.27
M^{relax}_{tot} (μ_B)	0.01	1.45	0.07	1.46
M^{relax}_{Fe} (μ_B)	0.01	1.56	0.06	1.63
E^{relax} (meV/atom)	-4.4	-2.7	-4.2	-3.1
$\Delta d^{1.NN}_{FeAl}$ (%)	4.10	3.22	4.07	3.62
$\Delta d^{2.NN}_{FeAl}$ (%)	-0.56	-0.39	-0.58	-0.55
$\Delta d^{3.NN}_{FeAl}$ (%)	0.80	0.59	0.81	0.78
$\Delta d^{4.NN}_{FeAl}$ (%)	0.16	0.12	0.16	0.17
$\Delta d^{5.NN}_{FeAl}$ (%)	-0.02	-0.02	-0.02	-0.02
$\Delta d^{6.NN}_{FeAl}$ (%)	0.21	0.11	0.24	0.25

Table I represents our results for the magnetic moment per Fe atom, for the gain in energy E^{relax} after structural relaxation, and for the radial shifts of the surrounding Al atoms due to the structural relaxation. The respective structure was relaxed until the force on each atom in the supercell was lower than 1 mRy/a.u. As in the former calculations,[1] the LSDA yields a magnetic moment ($1.63\mu_B$ at the Fe atom and in total $-0.01\mu_B$ at all the Al atoms) if the structural relaxation is neglected. However, this moment vanishes after structural relaxation which leads to a radial shift of the nearest-neighbor atoms of about 4% of the nearest-neighbor distance. For the GGA calculation the lattice constant is larger and now the structural relaxation with similar resulting atom shifts as in LSDA reduces the magnetic moment but does not lead to a total collapse. This is in line with the LSDA calculations of Ref. 2. In the latter calculation, the corresponding authors have shown that much larger shifts of the surrounding atoms are required for a collapse of the Fe moment when working at the experimental lattice constant (which is close to the GGA lattice constant) rather than at the considerably smaller LSDA lattice constant.

In the GGA calculation the structural relaxations are slightly smaller than those obtained in LSDA. For instance, the relaxations of the nearest-neighbor Al atoms towards the central Fe atom are 4.1% of the nearest-neighbor distance in the unrelaxed fcc structure in the case of LSDA, whereas this value is reduced to 3.2% in GGA-PBE (see Table I).

According to Anderson,[25] for magnetic transition-metal impurities with on-site U in a nonmagnetic metallic host there should be always a local magnetic moment in mean-field theory when U exceeds a critical value ($U>U_c$). Rigorously, below the Kondo temperature T_K such a moment will be suppressed by spin fluctuations which is, of course, beyond the calculations in a static limit.

In the LDA+U calculations (performed at the LSDA lattice constant) we obtained similar structural relaxations as in the LSDA and the GGA calculations, both for the AMF and the FLL versions, but with subtle marginal differences. More than the FLL version, the AMF version resembles the quantitative relaxation behavior seen in LSDA. In the FLL version, the nearest-neighbor relaxation lies between the LSDA and GGA-PBE values, although the relaxations of the far distant Al atoms resemble more the LSDA relaxations. Whereas there are only these minor differences in the structural relaxation behavior, also reflected in the small differences between respective energy gains, the description of the magnetic behavior becomes qualitatively different for the two LDA+U versions. Whereas the AMF version leads to a nearly complete collapse of the magnetic moment for the relaxed structure as the LSDA calculation, there remains a considerable magnetic moment similar to the one of the GGA calculation when working with the FLL version. When increasing U to 4 eV, a local moment can be stabilized also for the AMF version, in line with Anderson's work.

V. CONCLUSIONS

Both our present LDA+U calculations and the ones of Ref. 6 reveal that electronic correlations may be essential for the description of the intimate interplay between structure, energetics, and magnetism in some Fe-Al subsystems. In the present paper we applied the two currently used versions of the LDA+U method, AMF and FLL, to investigate two Fe-Al subsystems, the compound Fe_3Al and the Fe impurity in fcc-Al. The two versions yield coherent results concerning the energetical stabilization of the $D0_3$ structure of Fe_3Al against the $L1_2$ structure. For several structural properties, however, the results are sometimes quite different. Concerning the magnetic properties it can be stated that the AMF version tends to reduce the magnetic moments, at least for moderate values of U, as compared to the FLL version. This should be taken into account when the LDA+U method is applied to $3d$ transition metals or their alloys with moderate electronic correlations.

To conclude, the present LDA+U calculations and those of Ref. 6 have shown that correlation effects beyond the horizon of the approximate exchange-correlation functionals of LSDA and GGA are probably important for the Fe-Al system, even on a qualitative level. The LDA+U method which was originally designed for insulating systems with very strong correlations can be used to figure out the general importance of correlation effects also for metallic systems with moderate correlations such as Fe-Al, but the two currently used versions of this method are certainly not able to yield quantitative reliable results in this case.

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[1] N. Papanikolaou, R. Zeller, P.H. Dederichs, and N. Stefanou, Comput. Mater. Sci. **8**, 131 (1997).

[2] P.G. Gonzales, L.A. Terrazos, H.M. Petrilli, and S. Frota-Pessôa, Phys. Rev. B **57**, 7004 (1998).

[3] J. Bogner, W. Steiner, M. Reissner, P. Mohn, P. Blaha, K. Schwarz, R. Krachler, H. Ipser, and B. Sepiol, Phys. Rev. B **58**, 14 922 (1998).

[4] V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B **44**, 943 (1991).

[5] A.I. Liechtenstein, V.I. Anisimov, and J. Zaanen, Phys. Rev. B **52**, 5467 (1995).

[6] P. Mohn, C. Persson, P. Blaha, K. Schwarz, P. Novák, and H. Eschrig, Phys. Rev. Lett. **87**, 196401 (2001).

[7] H. Eschrig (private communication).

[8] M. Fähnle, J. Mayer, and B. Meyer, Intermetallics **7**, 315 (1999).

[9] F. Lechermann, F. Welsch, C. Elsässer, C. Ederer, M. Fähnle, J.M. Sanchez, and B. Meyer, Phys. Rev. B **65**, 132104 (2002).

[10] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997).

[11] T. Beuerle, K. Hummler, C. Elsässer, and M. Fähnle, Phys. Rev. B **49**, 8802 (1994).

[12] A.G. Petukhov, I.I. Mazin, L. Chioncel, and A.I. Lichtenstein, Phys. Rev. B **67**, 153106 (2003).

[13] G.Y. Guo, G.A. Botton, and Y. Nishino, J. Phys.: Condens. Matter **10**, L119 (1998).

[14] M.T. Czyżyk and G.A. Sawatzky, Phys. Rev. B **49**, 14 211 (1994).

[15] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyżyk, and G.A. Sawatzky, Phys. Rev. B **48**, 16 929 (1993).

[16] A.B. Shick, A.I. Lichtenstein, and W.E. Pickett, Phys. Rev. B **60**, 10 763 (1999).

[17] I.V. Solovyev, P.H. Dederichs, and V.I. Anisimov, Phys. Rev. B **50**, 16 861 (1994).

[18] J.P. Perdew, R.G. Parr, M. Levy, and J.L. Balduz Jr., Phys. Rev. Lett. **49**, 1691 (1982).

[19] D. J. Singh, *Planewaves, Pseudopotentials and the LAPW Method* (Kluwer Academic, Boston, 1994).

[20] B. Meyer, C. Elsässer, F. Lechermann, and M. Fähnle, *FORTRAN90 Program for Mixed-Basis-Pseudopotential Calculations for Crystals* (Max-Planck-Institut für Metallforschung, Stuttgart).

[21] M. Fähnle, C. Elsässer, and H. Krimmel, Phys. Status Solidi B **191**, 9 (1995).

[22] B. Meyer, Ph.D. thesis, University of Stuttgart, 1998.

[23] J.P. Perdew and Y. Wang, Phys. Rev. B **45**, 13 244 (1992).

[24] S.J. Pickart and R. Nathans, Phys. Rev. **123**, 1163 (1961).

[25] P.W. Anderson, Phys. Rev. **124**, 41 (1961).