



2003

Magnetic properties of Al, V, Mn, and Ru impurities in Fe–Co alloys

B. V. Reddy

Chrysalis Technologies Incorporated

S. C. Deevi

Chrysalis Technologies Incorporated

S. N. Khanna

Virginia Commonwealth University

Follow this and additional works at: http://scholarscompass.vcu.edu/phys_pubs

 Part of the [Physics Commons](#)

Reddy, B. V., Deevi, S. C., Khanna, S. N. Magnetic properties of Al, V, Mn, and Ru impurities in Fe–Co alloys. *Journal of Applied Physics* 93, 2823 (2003). Copyright © 2003 AIP Publishing LLC.

Downloaded from

http://scholarscompass.vcu.edu/phys_pubs/128

This Article is brought to you for free and open access by the Dept. of Physics at VCU Scholars Compass. It has been accepted for inclusion in Physics Publications by an authorized administrator of VCU Scholars Compass. For more information, please contact libcompass@vcu.edu.

Magnetic properties of Al, V, Mn, and Ru impurities in Fe–Co alloys

B. V. Reddy^{a)} and S. C. Deevi

Research Center, Chrysalis Technologies Incorporated, P.O. Box 37310, Richmond, Virginia 23234

S. N. Khanna

Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284-2000

(Received 23 July 2002; accepted 9 December 2002)

Theoretical studies on the magnetic properties of impurities in Fe–Co alloys have been carried out using a molecular-orbital approach within a gradient corrected density functional formalism. The defected alloy is modeled by a large cluster and the calculations on the ordered alloy are used to show that a cluster containing 67 atoms can provide quantitative information on the local magnetic moment. It is found that although bulk Al, V, and Ru are nonmagnetic, all the impurities carry finite moments. While Al and V impurities couple antiferromagnetically, Ru impurities couple ferromagnetically to the host sites. It is shown that the observed composition dependence of the rate of increase of magnetic moment of $\text{Fe}_x\text{Co}_{1-x}$ alloys upon addition of Mn impurities is due to the change in the magnetic moment of Mn impurities with composition. The reasons for this change and the possibility of stabilizing a higher Mn moment at all concentrations are discussed. © 2003 American Institute of Physics. [DOI: 10.1063/1.1541109]

I. INTRODUCTION

Several problems in condensed matter physics require knowledge of the local properties. This includes problems such as impurities, vacancies, and voids in solids; atoms located or adsorbed on surfaces, and disordered materials. One is interested in knowing the local magnetic moment and the density of states, location of the impurity, relaxations around the impurity, and the effect on the local surroundings. While many of these problems can be studied by using supercells in the conventional band structure formalisms, an accurate treatment of the defected region requires local relaxations that can be computationally difficult.¹ An alternate approach that is gaining considerable attention is to model the solid by a large cluster.² The real space electronic structure schemes adapted to clusters where the geometries can be optimized without regard to symmetry or periodicity can be used to obtain the desired information. Indeed, over the past few years, numerous studies of the solid-state phenomena using model clusters have been carried out. Since the surface sites in a free cluster have fewer neighbors than the bulk, one of the nagging questions facing such an approach has been the smallest cluster size that is needed to model the local site. The problem becomes more complex in the case of alloys since one has to worry about the atomic composition in addition to the size. The limitations in the cluster size over which *ab initio* cluster calculations could be carried out have generally prevented a definite answer.

In this article, we propose to carry out theoretical studies on pure and impurity doped FeCo alloys using cluster models. These alloys exhibit the highest saturation magnetization (in transition metal systems) and are well known for applications as soft magnetic materials.³ While the highest satu-

ration magnetization occurs around 35% Co, the equiatomic Fe–Co alloy has a higher permeability and a Curie temperature of around 1200 K and is widely used in magnetic applications. One of the most interesting aspects of the bulk alloy is the behavior of the impurity atoms.⁴ It is found that while Ti, V, and Cr impurities order antiferromagnetically, the Mn and Ni order ferromagnetically. The case of Mn is particularly interesting since bulk Mn exhibits complex antiferromagnetic arrangement while Mn clusters have been recently found to exhibit ferromagnetic order.⁵ Experiments show that while the addition of Mn leads to a decrease of the average moment for alloys with higher Fe content than Co, the effect is reversed for alloy compositions richer in Co. The increase in average moment in Co rich alloys is particularly intriguing since Mn impurities in pure Co order antiferromagnetically to the host sites.⁴ How the Mn moment and coupling change with the relative concentration of Fe and Co remains an open issue. Since the cluster techniques are ideally suited to probe local properties, it is interesting to study the magnetic behavior of various impurities and their effect on local properties.

The main objective of the present work is to examine the local magnetic moment of the various substitution impurities in these alloys. We have chosen as impurities, a simple metal Al, the 3*d* transition elements V and Mn, and the 4*d* transition metal Ru in this study. As we use a cluster model to simulate the bulk behavior, the first issue we wish to address is the minimum cluster size that can provide a quantitative estimate of the local magnetic moment at the Fe or Co site in an ordered FeCo alloy. By studying clusters containing 15, 35, and 67 atoms, we show that a cluster containing at least up to several third nearest neighbors of the given site is needed to obtain quantitatively converged local magnetic moments. Accurate neutron diffraction experiments⁶ indicate that while the Fe moment increases with Co concentration from 2.2 μ_B in pure Fe to 2.92 μ_B in the Fe–Co alloy, the Co moment remains essentially constant. It is shown that the

^{a)} Author to whom correspondence should be addressed; electronic mail: budda.v.reddy2@pmusa.com

converged cluster results are close to the experimental values. These clusters are then employed to examine the location of the impurities and their local properties. It is found that all the impurities preferentially occupy the Fe sites. In the case of Al, V, and Ru that are nonmagnetic in bulk, the impurities carry local moments of 0.31, 0.62, and 1.43 μ_B , respectively. While Al and V couple antiferromagnetically, the Ru impurities couple ferromagnetically to the host polarization. For the Mn impurities, we find that while they order antiferromagnetically in pure Co, they order ferromagnetically in Fe–Co alloys with a Mn moment that changes with the relative concentration of Fe and Co.

The article is organized as follows. In Sec. II we give the details of the electronic structure methods and the clusters used to model the bulk behavior. Section III contains the results of investigations on pure clusters and the magnetic state of impurities in FeCo alloys. Finally, Sec. IV is dedicated to final conclusions.

II. DETAILS OF CALCULATIONS

The theoretical calculations were carried out using a linear combination of atomic orbitals molecular orbital approach within a density functional formalism.⁷ Here, the molecular orbitals are formed by a linear combination of atomic orbitals centered at the atomic sites. The exchange correlation effects are incorporated through a gradient corrected density functional.⁸ The actual calculations were carried out using the DMOL code⁹ where the atomic orbitals are taken in a numerical form over a mesh of points. All the calculations were carried out at an all electron level using double numerical basis sets with 3*d* polarization functions for Al, 4*p* polarization functions for V and Mn, and 5*p* polarization functions for Ru. In all cases, we examined the ferromagnetic and antiferromagnetic solutions.

We start with the ordered Fe–Co alloy. We have carried out studies on 15, 35, and 67 atom clusters shown in Fig. 1. In each case we carried out calculations on clusters with a Fe atom at the center and the reciprocal clusters with Co located at the center. For convergence of the cluster results, we not only looked at the convergence with respect to the increasing size but also examined the moment at the Fe and Co sites in the central core of the reciprocal clusters. The 15-atom cluster contains all the nearest neighbors of the central site and has eight Fe (Co) and seven Co (Fe) atoms. The 35-atom cluster has all the nearest neighbors of the first neighbors of the central site and has 27 Fe (Co) and eight Co (Fe) sites. The next size that includes almost all the nearest neighbors of the second neighbors contains 67 atoms. It has 27 Fe (Co) and 40 Co (Fe) sites. For all the clusters, the interatomic distances were optimized by moving atoms in the direction of forces.

III. RESULTS AND DISCUSSION

A. Effect of size on the local magnetic moments in Fe_nCo_m clusters

In Table I we list the local magnetic moments at various sites of the clusters shown in Fig. 1. We start with the results on 15 atom clusters shown in Fig. 1(a). The central Fe site is

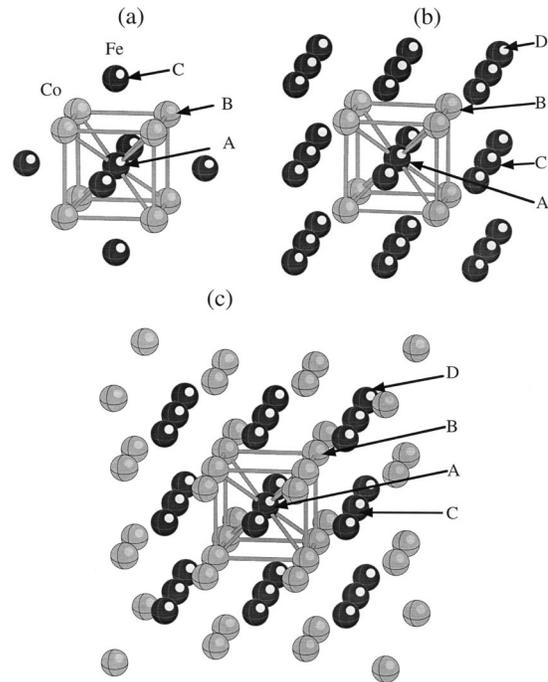


FIG. 1. Geometries of 15, 35, and 67 atom FeCo clusters. The Fe sites are shown by the dark circles while the lighter shades are the Co atoms. The reciprocal clusters are obtained by interchanging Fe and Co sites.

surrounded by eight Co atoms that are further decorated with six Fe atoms. In the optimized cluster, the distance between the central Fe and the nearest Co is 2.32 Å. Our studies show that the central Fe has a moment of 2.51 μ_B while the surrounding Co atoms have moments of 1.76 μ_B each. The outer Fe atoms have moments of 3.23 μ_B . In the reciprocal cluster with Co at the center, the central Co has a moment of 1.72 μ_B , while the Fe sites have moments of 3.37 μ_B . The outermost Co had moments of 2.06 μ_B . Note the considerable difference in the moment of Fe sites located at the cen-

TABLE I. The central Fe–Co distance (Å) and the magnetic moment at the central and surrounding sites in Fe–Co clusters of various sizes. Sites A, B, C, and D are marked in Fig. 1.

Cluster	Fe–Co distance	Local magnetic moment (μ_B) at			
		A	B	C	D
FeCo_8Fe_6	Bulk	3.01	2.14	3.37	...
	2.32	2.51	1.76	3.23	...
$\text{FeCo}_8\text{Fe}_{26}$	Bulk	2.72	1.32	3.13	3.19
	2.31	2.59	1.29	3.21	3.19
$\text{FeCo}_{40}\text{Fe}_{26}$	Bulk	2.91	1.70	2.89	3.12
	2.40	2.71	1.53	2.79	3.07
CoFe_8Co_6	Bulk	1.74	3.38	2.04	...
	2.39	1.72	3.37	2.06	...
$\text{CoFe}_8\text{Co}_{26}$	Bulk	1.38	2.65	1.87	2.15
	2.35	1.45	2.54	1.93	2.16
$\text{CoFe}_{40}\text{Co}_{26}$	Bulk	1.60	2.93	1.56	1.81
	2.41	1.63	2.91	1.56	1.78

ter and at the first layer (Fig. 1). This shows that one needs to go to larger clusters in order to get converged moments at the Fe or Co site.

The 35-atom cluster shown in Fig. 1(b) offers the next bigger size. The distance between the central Fe and nearest Co is 2.31 Å and Fe has a magnetic moment of 2.59 μ_B . The surrounding Co have moments of 1.29 μ_B . The Fe–Co distance in bulk alloy is 2.47 Å and the corresponding moments at the Fe and Co site in the cluster at the bulk spacing were 2.72 and 1.32 μ_B , respectively. We also studied the reciprocal cluster. The central Co had a moment of 1.45 μ_B while the nearest Fe had moment of 2.54 μ_B . The Co–Fe distance was 2.35 Å. The corresponding moments at the central Co and Fe site in reciprocal clusters with bulk lattice spacing were 1.38 and 2.64 μ_B , respectively. These results bring out two important features. First, that the magnetic moment on the Fe or Co change appreciably with size and location. The calculated values are considerably different from the experimental values⁶ of 2.92 and 1.62 μ_B for the Fe and Co moment, respectively. Second, the moments seem to change mildly with lattice relaxation.

We then examined 67 atom clusters shown in Fig. 1(c). The interatomic distances were optimized by moving atoms in the direction of forces. In the cluster 1(c), the central Fe had a moment of 2.71 μ_B while the Co had a moment of 1.53 μ_B . In the reciprocal cluster, the central Co had a moment of 1.63 μ_B while the Fe had a moment of 2.91 μ_B . This shows that the Fe and Co moments are not sensitive to whether Fe or Co is at the central site, indicating a convergence with respect to cluster size. The present calculated moments of 2.71 and 1.6 μ_B are comparable to the corresponding experimental⁶ moments of 2.92 and 1.62 μ_B . It is interesting to note that the recent band structure calculations^{10,11} reported the Fe and Co moments of 2.69 and 1.67 μ_B , respectively, that are also close to the current values. To further ascertain that 67 atom clusters do lead to quantitatively accurate results, we carried out similar calculations on pure Fe for which the spin magnetic moment is accurately known. The central Fe in the pure Fe cluster had a moment of 2.03 μ_B compared to the experimental value of 2.11 μ_B . All these results indicate that in order to get quantitatively accurate magnetic moments using cluster models, one needs to go to cluster sizes including beyond second neighbors.

B. Magnetic moment of impurities in Fe–Co alloys

As mentioned before, our primary interest is to obtain the location and the magnetic configuration of impurities in Fe–Co alloys. As we have shown in a previous article,¹² clusters containing smaller sizes can provide qualitative information as to the location of the impurity and the nature of magnetic coupling. This suggests that a dual approach where one carries out geometry optimization on smaller sizes to obtain the location of impurities and their coupling and uses this information in a bigger cluster to obtain accurate local moments provides a viable alternative. This is the approach we have used.

An impurity can occupy the Fe or the Co site. To find the preferred site, we chose the clusters shown in Fig. 1(b) and

TABLE II. Nature of magnetic coupling [ferromagnetic (FM), antiferromagnetic (AFM)] and the local magnetic moment (μ_B) at the impurity μ_{imp} and the nearest neighbor Co site μ_{Co} in the 67 atom clusters.

Impurity	Coupling	μ_{imp}	μ_{Co}
Al	AFM	0.31	1.41
V	AFM	0.62	1.38
Mn	FM	3.11	1.50
Ru	FM	1.43	1.60

its reciprocal counterpart. To examine whether the impurity will occupy the Fe or Co site, we calculated the change in energy of the pure clusters when an impurity atom replaces the central site. The preferential site then corresponds to the case where either the energy is gained or where the energy required to replace the central Fe (Co) site is lower. In each case, all the atoms were relaxed and both ferromagnetic and antiferromagnetic arrangements were examined.

In this work we have examined Al, V, Ru, and Mn impurities. Except for V, the binding energy was lowered as the impurity was substituted at the central site. In the case of V, the binding energy increased. This indicates that only for V, the substitution is energetically favorable. A comparison of the relative energies for occupying the Fe and Co sites indicated that all impurities prefer to occupy the Fe sites. The relative energy difference between the impurity occupying the Co or the Fe site was 1.25, 1.03, 0.93, and 0.94 eV for Al, V, Ru, and Mn, respectively. As mentioned before, we are primarily interested in the magnetic state of the impurity and its effect on the local magnetic moment. To this end, we carried out calculations on 67 atom clusters with the central Fe replaced by the impurity atoms. Table II presents our results on the nature of coupling between the impurity and the host atoms and the local magnetic moment at the impurity and the surrounding sites. Note that since all the impurities prefer Fe sites, the nearest surrounding atoms are always the Co atoms. Bulk Al and V are nonmagnetic. However, the Al and V impurities have local moments of 0.3 and 0.62 μ_B , respectively. Note that in both cases, the local moments are aligned antiferromagnetically to the surrounding Co atoms whose moments are slightly reduced from the pure cluster value of 1.53–1.46 and 1.38 μ_B , respectively. For the case of V, the antiferromagnetic coupling and the reduction of the moment of the surrounding Co sites is in agreement with experiments⁴ that indicate a large decrease in magnetization upon addition of V impurities. The Ru atoms, on the other hand, couple ferromagnetically to the host atoms and carry a moment of 1.43 μ_B .

As mentioned before, the case of Mn is particularly interesting.^{4,5} For alloys with more than 50% Fe, the Mn substitution leads to a decrease of the average magnetic moment while the average magnetic moment increases at equiatomic and higher Co content. Note that at equiatomic composition, the Mn site has only Co near neighbors. For Fe concentrations of more than 50%, the nearest neighbors to the Mn site would contain one or more Fe atoms. Since bulk FeMn is antiferromagnetic, one could imagine that the presence of nearest Fe atoms leads to an antiferromagnetic coupling of the Mn sites. Another possibility is that the coupling

TABLE III. The one-electron eigenvalues in $\text{MnCo}_8(\text{MnFe}_8)$ clusters with appreciable d contribution from the Mn site. The corresponding representation, spin, and the Mulliken charge on the Mn sites are also listed.

MnCo_8				MnFe_8			
Eigenvalues (eV)	Representation	Spin	Charge (e^-)	Eigenvalues (eV)	Representation	Spin	Charge (e^-)
-7.32	E_g	Up	0.57	-7.16	E_g	Up	0.49
-3.81	E_g	Up	1.08	-3.58	E_g	Up	1.15
-7.05	T_{2g}	Up	1.15	-6.68	T_{2g}	Up	0.87
-3.50	T_{2g}	Up	1.00	-3.24	T_{2g}	Up	0.72
-5.70	E_g	Down	0.58	-5.37	E_g	Down	0.83
-5.71	T_{2g}	Down	1.20	-5.46	T_{2g}	Down	1.56

remains ferromagnetic but the Mn moment gradually decreases and becomes smaller than the Fe moment, leading to an overall decrease as the Mn occupies Fe sites. To examine these possibilities, we have carried out calculations on $\text{MnFe}_{26}\text{Co}_8$, and $\text{MnFe}_{30}\text{Co}_4$ clusters. The former represents a single Mn impurity in equiatomic alloy, while the later corresponds to a Mn impurity in the Fe rich alloy. In each case the ferromagnetic and antiferromagnetic solutions were tried.

We start with the $\text{MnFe}_{30}\text{Co}_4$ cluster corresponding to a low Co concentration in $\text{Fe}_x\text{Co}_{1-x}$ alloy and we find that the Mn atoms exhibit local moments less than $0.1 \mu_B$. Note that the addition of Mn in these alloy compositions will lead to a lowering of the overall moment since the Mn moment is substantially smaller than the Fe moment. This is in agreement with experiments. The cluster $\text{MnFe}_{26}\text{Co}_8$ correspond to a Mn impurity in the equiatomic FeCo alloy and here the Mn site is found to couple ferromagnetically with a local moment of $3.06 \mu_B$. Since the Mn moment is now higher than the moment at the Fe site, any addition of Mn should lead to an enhancement of the average magnetic moment. This is in agreement with experiments⁴ that confirm an increase of magnetic moment upon addition of Mn! Combined, these results indicate that as opposed to the case of pure Co, the Mn impurities always couple ferromagnetically to the host sites even though the Mn has only Co near neighbors. The magnitude of the Mn moment, however, changes with composition and is responsible for the decrease/increase of average moment with concentration.

In order to explore if the nature of coupling of Mn sites can be understood at a rudimentary level, we have carried out model calculations on MnFe_8 and MnCo_8 clusters consisting of a central Mn surrounded by a cube of eight Fe (Co) neighbors. In MnFe_8 , the Mn and the Fe sites have local moments of 0.48 and $3.32 \mu_B$, respectively. We also found a solution where the Mn is coupled antiferromagnetically with a local moment of $-0.15 \mu_B$, to be 0.1 eV less stable than the ferromagnetic solution. Anisimov *et al.*¹³ have studied Mn impurities in bulk Fe using the linear-muffin-tin-orbital Green's function method and find two solutions with a local magnetic moment on Mn of -2.30 and $1.60 \mu_B$, respectively. These calculations were carried out at the experimental bulk lattice spacings and no relaxation of the local atoms surrounding the impurity was permitted. It is therefore difficult to compare their results with present studies that include relaxation. For MnCo_8 , the present studies indicate that Mn

and Co have local moments of 2.05 and $2.12 \mu_B$, respectively. The key is to note that while in all cases, the Mn moment is reduced from its free atom value, Mn has a higher moment when attached to Co sites than when attached to Fe sites. Almost all the magnetic moment is derived from d electrons and the reason for this difference can be roughly understood within a simple bonding scheme involving d electrons. Note that Mn, Fe, and Co, all have filled majority $3d$ and $4s$ levels while the minority spin $3d$ levels have 0, 1, and 2 electrons, respectively. As these atoms bond together, the minority d -bonding orbitals become more stable than the majority d -antibonding orbitals. This results in a transfer of the majority spins to the minority spins. When coupled to Fe that has only 1 minority $3d$ spin electron and a $4s$ spin electron, the transfer of majority $3d$ electrons on the Mn site is more than in the case of Co which has two electrons in the minority $3d$ and one in the $4s$ level. The free atom Mn moment then undergoes enhanced quenching in Fe rather than in the case of Co. This is clearly seen in Table III where we have listed the eigenvalues with appreciable d contribution from the Mn site along with the Mulliken charge from the Mn d electrons. Note that the minority spin has more charge from Mn in the case of MnFe_8 than in the case of MnCo_8 . We would like to add that the Mn impurities in pure Co are known to couple antiferromagnetically while the Mn impurities in high Co content FeCo alloys couple ferromagnetically. The reason for this lies in the atomic arrangement. Pure Co has a hexagonal closed packed structure and it is possible that the Mn impurities in such an arrangement of Co atoms couple antiferromagnetically to Co sites. Further studies to examine the effect of geometrical order on the local coupling are in progress.

IV. CONCLUSIONS

To conclude, we examined various impurities in FeCo alloys and have shown that the impurities prefer to occupy Fe sites. Further, although bulk Al, V, and Ru are nonmagnetic, their impurities in FeCo alloys do carry finite magnetic moments. For the case of Al and V, the impurities order antiferromagnetically but the Ru impurities order ferromagnetically. For Mn, we have shown that the impurities order ferromagnetically but the local moment changes with the composition. For alloys with equiatomic and higher Co content, the local moment at the Mn sites is higher than the Fe moment of 2.71 and is responsible for the increase in the

magnetization of FeCo alloys by adding Mn in low content as observed in some previous works. What the present studies show is that the increase of magnetization via addition of Mn could even continue at other concentrations provided the Mn sites can be locally surrounded by Co nearest neighbors. How to reduce this in practice, however, remains an open issue.

- ¹T. P. Das, in *Electronic Properties of Solids Using Cluster Methods*, edited by T. A. Kaplan and S. D. Mahanti (Plenum, New York, 1995), pp. 1–28.
- ²J. L. Whitten, in *Cluster Models for Surface and Bulk Phenomena*, edited by G. Pacchioni and P. S. Bagus (Plenum, New York, 1992), p. 375.
- ³S.-Y. Chu, C. Kline, M.-Q. Huang, M. E. McHenry, J. Cross, and V. G. Harris, *J. Appl. Phys.* **85**, 6031 (1999).

- ⁴*Magnetism and Metallurgy of Soft Magnetic Materials*, edited by C.-W. Chen (North Holland, New York, 1977).
- ⁵M. B. Knickerbein, *Phys. Rev. Lett.* **86**, 5255 (2001).
- ⁶E. Di. Fabrizio, B. Mazzone, C. Petrillo, and F. Sacchetti, *Phys. Rev. B* **40**, 9502 (1989).
- ⁷W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ⁸A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988); A. D. Becke, *J. Chem. Phys.* **88**, 2547 (1988); J. P. Perdew *et al.*, *Phys. Rev. B* **46**, 6671 (1992).
- ⁹B. Delley, *J. Chem. Phys.* **92**, 508 (1990).
- ¹⁰S. L. Qiu, P. M. Marcus, and V. L. Moruzzi, *J. Appl. Phys.* **85**, 4839 (1999).
- ¹¹J. M. MacLaren, T. C. Schulthess, W. H. Butler, R. Sutton, and M. McHenry, *J. Appl. Phys.* **85**, 4833 (1999).
- ¹²B. V. Reddy, D. H. Sastry, S. C. Deevi, and S. N. Khanna, *Phys. Rev. B* **64**, 224419 (2001).
- ¹³V. I. Anisimov, V. P. Antropov, A. I. Liechtenstein, V. A. Gubanov, and A. V. Postnikov, *Phys. Rev. B* **37**, 5598 (1988).