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luizno.bjp@gmail.com
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Paduani, C.; Krause, J. C.
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A First-Principles Study of Cr Impurities in Iron.

C. Paduani
Departamento de Física,
Universidade Federal de Santa Catarina,
UFSC, Florianópolis, CEP 88040-900, SC, Brazil

and J. C. Krause
Universidade Regional Integrada do Alto Uruguai e Missões,
DCET-URI, Santo Ângelo, CEP 98802-470, RS, Brazil

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The first-principles molecular cluster discrete variational method (DV) is used to investigate the electronic structure and local magnetic properties of Cr impurities in bcc iron and Fe/Cr interfaces. The spin polarized case is considered within the framework of the local-spin-density approximation of the density function theory. The effect on the local moment and hyperfine magnetic field (Fermi contact term) of adding Cr atoms in the vicinity of Fe atoms is investigated. For a Cr impurity in bcc iron the calculated magnetic moment and hyperfine field is -0.62 μ_B and -300 kG, respectively. For pure chromium we obtained -0.49 μ_B and -67 kG. The Fe moment is sensitive to the separation between Cr atoms in the first shell of neighbors.

Keywords: Iron-chromium alloys; Hyperfine field; Magnetic properties; Electronic structure; Transition metals

I. INTRODUCTION

The Fe-Cr alloy system has the bcc structure (CsCl - B_2) in the whole range of composition[1] and is a model system to study giant magnetoresistance. Pure bcc Cr has a magnetic structure with transverse or longitudinal spin density waves depending on the temperature. Experimental results have shown that chromium is antiferromagnetic (AF) with T_N = 233 K with a magnetic moment per atom of 0.45 μ_B [2]. The low temperature local magnetic moments describe an AF spin-density wave with a maximum value of 0.59 μ_B , corresponding to an average value of 0.43 μ_B [3]. A magnetic moment of 0.62 μ_B has also been reported for bulk Cr[4]. Results of magnetic measurements show that Cr nanoparticles exhibit mainly AF properties, in addition to a weak-ferromagnetic component at lower fields, which may be ascribed to uncompensated surface spins[5]. In Cr-rich Fe-Cr alloys, experimental results have indicated that the average magnetic moment per atom increases rapidly with increasing iron concentration[3, 6, 7]. For the Cr impurity in iron a moment of -0.9 μ_B has been reported from neutron diffraction measurements[8, 9]. For pure chromium, neutron diffraction has also indicated an antiphase domain structure, where at regular intervals in the lattice there is a reversion in the direction of orientation for the spin moments. In layered Fe/Cr structures the thickness dependence of the Cr magnetic moment has been investigated by magnetic linear dichroism[10]. It has been verified a decrease of the overall magnetic moment in the Cr layer by increasing thickness. Besides, in amorphous Cr-Fe alloys obtained by thermal evaporation and mechanical milling it has been observed that amorphization causes a strong reduction of Fe moment [11].

Total-energy band-structure calculations in the local-spin-density approximation utilizing a fixed-spin-moment procedure indicated that chromium undergoes a first-order transition from nonmagnetic to magnetic behavior at expanded volumes[12, 13]. For the Cr impurity in iron calculated results for the magnetic moment and hyperfine magnetic field yielded -0.9 μ_B and -136.3 kG, respectively. In multilayers both theoretical and experimental results have indicated a decrease of the magnetic moments for interfacial atoms as well as enhanced moments for the inner atoms.[14–16] Results from an energy analysis of the magnetic order and interlayer relaxation in *ab initio* calculations for transition metal monolayers on the Fe(001) substrate indicated that Cr prefer the layered AF coupling.[17].

In this work we present a detailed investigation of the magnetic properties of Cr impurities in bcc iron and layered structures, in non-relativistic spin-polarized electronic structure calculations by using the molecular cluster discrete variational method[18]. The calculations apply the density-function theory using the local spin density approximation of von Barth-Hedin[19]. A collinear spin structure was considered and no lattice relaxation has been taken into account. The calculations were performed with the experimental value for the bcc lattice spacing. We check the reliability of this cluster method and of the LSDA approach to describe the magnetism of ferromagnetic Fe-Cr alloys by comparing our results with available experimental data.

II. CALCULATIONAL DETAILS

In this method a linear combination of atomic orbitals is used to built up the molecular orbitals, and the numerical atomic orbitals are generated by solving the atomic problem. A spherically averaged potential is used around each atom in order to obtain more contracted valence orbitals in the cluster region. The molecular clusters were built up with the experimental value of 5.416 a.u. of bcc iron. The origin of coordinates is at the body centered site. The central atom in the cluster has complete coordination like that of bulk atoms.

The microcrystal was extended up to 40 a.u. including about 2400 atoms. The embedding scheme is well-described elsewhere in the literature. The adopted superstructures are: (i) a Fe/Cr interface, where the atoms in the $z = 0$ and the lower planes are Fe atoms; (ii) a Cr/Fe interface, with a plane of Cr atoms at $z = 0$;(iii) a Cr monolayer (plane Cr at $z = 0$), and (iv) three Cr layers, consisting of three planes of Cr atoms, with the middle plane of Cr atoms at $z = 0$. A minimal basis was adopted in this case, which includes 1s-4p orbitals for both iron and chromium. The matrix elements of the Hamiltonian and overlap are evaluated by direct numerical integration procedures, using a random sampling method, where a sum of Fermi-type functions around each atom is adopted as the distribution function of the sample points. The non-zero spin density of electrons-s at the nucleus ($\Delta\rho_S(0)$) gives rise to the Fermi contact hyperfine field which can be obtained by

$$H_c = 524.3 \times \Delta\rho_S(0)\, kG.$$

III. RESULTS AND DISCUSSION

The 3d l-projected local density of states (LDOS) are shown in Fig. 1. The LDOS for bcc iron is shown in Fig. 1a and for an interfacial Fe atom in Fig. 1b. For pure Cr an AF coupling was considered for the magnetic configuration. For the interfacial Fe atom a decrease of the contribution from the spin-up subband is observed, considering that the population of the d-level is nearly the same in both cases. For the Interfacial Cr atom, in Fig. 1d one sees a strong reduction in the DOS at the Fermi level, as compared to pure chromium (Fig. 1c). The weight of the LDOS is shifted to lower energies, which indicates a stronger interaction between the localized d-electrons and the conduction electrons (as compared to pure chromium). As an isolated impurity, the Cr atom exhibit an enhanced polarization in the d-band, with a large contribution in the DOS at the Fermi energy, as can be seen in Fig. 1e. Further, for a monolayer (ML) of Cr atoms in this host, one sees in Fig. 1f how the states are accumulating near to the Fermi energy, which decreases thereby the hybridization with the s-states.

In Table 1 are shown the calculated results for the magnetic moment and contact hyperfine field for Fe atoms. Only the results for the central atom are shown in the table, since this is the probe atom which is expected to present bulk-like properties. For a single Cr impurity in the bcc iron host we obtained μ = -0.62 μ_B . For pure Cr a moment of -0.49 μ_B was obtained, which is in good agreement with experimental findings as well as with first-principles calculations of thermodynamic and magnetic properties of Fe-Cr alloys[21]. Earlier calculations with the KKR Green's function method yielded a Cr moment $\mu <$ -1 μ_B [20]. It is worth to mention also that spin-polarized first principles calculations with tight-binding linear muffin-tin orbital method have shown that the effect of different models of local exchange potentials on the Fe moment is negligible, whereas for bulk Cr, which is antiferromagnetic, the calculated magnetic moment strongly depends on the particular form of the potential as well as on the lattice constant used[4]. The Vosko-Wilk-Nusair parameterization gives a Cr moment similar to the experimental value only at the experimental lattice spacing.

As one sees in Table 1, the introduction of Cr atoms in the vicinity of a Fe atom leads to a decrease of the Fe moment. The Cr moment was found to be antiferromagnetically coupled to those of neighboring Fe atoms. A loss of polarization was observed for both conduction electrons and localized valence electrons. An effect which is indicated by our calculations is that the local Fe moment is rather sensitive to the separation between Cr atoms, an effect which becomes even stronger by increasing the number of nearest-neighbors (NN) Cr atoms. For instance, in Table 1 one sees that with 2 NN Cr atoms the Fe moment is larger when the Cr atoms are closer, as in the C_{2v} symmetry (see Fig. 2). The same trend is also observed with 4 NN Cr atoms. With 8 NN Cr atoms the calculated moment increases to 2.3 μ_B . It is worth to mention that, according to experimental results, the average magnetic moment per atom increases rapidly with increasing iron concentration in Cr-rich Fe-Cr alloys. This feature may be inferred from the present calculations, even though it could be also an artifact, since the lattice relaxation was not taken into account.

The polarization of the conduction band is much more strongly affected with the introduction of Cr atoms in the immediate neighborhood of Fe. The coupling between the localized d-electrons and the conduction electrons changes to ferromagnetic with 4 NN Cr atoms and increases thereafter. Our calculated result for the contact field of chromium is -67 kG, higher than the first experimental predictions, which indicate an upper limit of 13 kG [22]. For the Cr impurity in iron we obtained H_c= -300 kG, which agrees with experimental findings (≈ 277 kG)[9]. At a Fe/Cr interface the Fe moment

TABLE I: Calculated results for the local magnetic moment (μ) and the conduction band contribution (μ_c) $4s+4p$ (in μ_B), the Fermi contact field H_c (in kG) for Fe atoms with Cr atoms as nearest-neighbors (NN). Results for bulk Cr, a single Cr impurity, interfacial Fe and Cr atoms, a monolayer (ML) and 3 layers of Cr atoms in Fe are also included.

number of NN Cr atoms	μ	μ_c	H_c
		Fe	
0	2.19	-0.32	-320
1	1.92	-0.16	-226
2^a	2.08	-0.03	-226
2^b	1.81	-0.05	-199
4^c	1.98	0.16	-196
4^d	2.01	0.10	-226
8	2.30	0.38	-207
interfacial Fe	1.78	-0.06	-124
		Cr	
bulk Cr	-0.49	-0.03	-67
impurity Cr	-0.62	-0.47	-300
interface Cr	-0.31	-0.09	
ML Cr	-1.32	0.18	
3-layers Cr	-1.38	-0.21	

[a] C_{2v}
[b] D_{3d}
[c] T_d
[d] D_{2d}

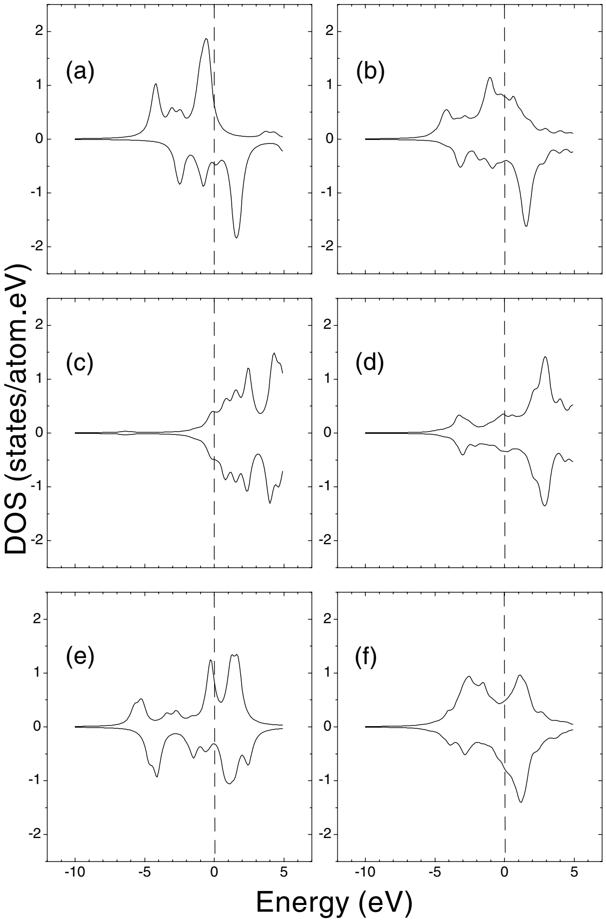

FIG. 1: 3d orbital projected LDOS for: (a) pure bcc Fe; (b) a Fe atom at a Fe/Cr interface; (c) bcc Cr; (d) a Cr atom at a Cr/Fe interface; (e) a Cr impurity in Fe; (f) a Cr monolayer in Fe. The negative DOS means spin down states. The vertical line indicates the Fermi level, which is shifted to the origin.

decreases, as compared to the bulk value. For an interfacial Cr atom the calculated moment is about half of that for a single impurity.

For 1 ML of Cr atoms an enhanced Cr moment was observed, as compared to a Cr impurity. For 3 Cr layers the Cr moment (at the middle layer) increases slightly, which indicates a tendency to obtain enhanced moments with the increase of the thickness of the Cr layers. According to spin-polarized FLAPW calculations for Cr(100)/Fe layers the Cr moment decreases as going from the surface to inner layers[23]. However, as pointed out by the authors this is not an effect of a finite slab thickness, and the deviation relative to experimental results is a consequence of using the experimental bulk lattice constant. Nevertheless, results of measurements with magnetic linear dichroism have shown a decrease of the magnetic moment for the Cr layer by increasing thickness, being that interfacial atoms have smaller moments than those at the inner layers[24]. Our calculations are in agreement with that picture. Enhanced moments relative to pure Cr have also been observed in first-principles calculations of Cr

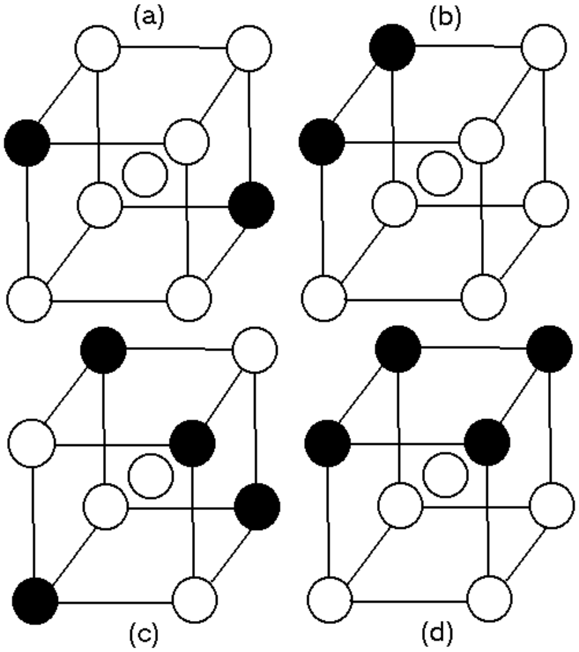

FIG. 2: Cr atoms (full circles) in a bcc unit cell of Fe atoms (open circles) for the symmetries: D_{3d} (a), C_{2v} (b), T_d (c) and D_{2d} (d).

impurities in overlayers on Fe(001) substrate[25].

The calculated magnetic hyperfine field (Fermi contact term) H_c for Fe atoms are also shown in Table 1. There one sees that, although H_c decreases with the introduction of NN Cr atoms, there is a strong effect which is arising from the interaction between the Cr atoms which affects the contact field. When the Cr atoms are farther apart from each other both local moment and H_c of Fe atoms are smaller. At the interface between two thick Fe and Cr slabs the hyperfine field of Fe atoms is strongly decreased, as compared to pure Fe and in dilute FeCr alloys. The sign of H_c is negative in all cases considered in the calculations. Nevertheless, the reduced coordination number for the magnetic coupling at the interfacial sites leads to an inversion of the contribution of the conduction electrons to the spin density of s-electrons at the iron nuclei, which causes the large decrease of H_c for the interfacial Fe atoms. As can be seen in Table 1, despite that similar values were obtained for both μ and μ_c for Fe at the interface, as well as with 2 NN Cr atoms in the D_{3d} symmetry, quite different values are observed for the hyperfine fields. In the source of this discrepancy is the much larger contribution from the conduction electrons to the spin density at the Fe nuclei in the D_{3d} symmetry. The results above indicate that H_c is strongly dependent on the local symmetry. As a further step to be investigated is the effect of lattice relaxation on these quantities.

IV. SUMMARY

Molecular cluster calculations were performed with the first-principles discrete variational method to investigate local magnetic properties of Fe-Cr alloys. The results of the calculations indicate that the s-electron polarization at a given Fe site depends not only on the moment at that site but also on the distribution of moments in its vicinity (chemical environment) as well as on the local symmetry. The conduction electrons contribution to the spin density at the iron nuclei decreases for sites which have a Cr impurity as a nearest neighbor, since the local moment on the Cr impurity is always smaller than that of pure Fe. This feature has also been verified in other transition metal dilute alloys [9]. Moreover, our results indicate that in multilayers the conduction electrons polarization is sensitive to the number of Cr layers and even changes sign with the increase of the layer thickness. At the interface, similar contributions from the conduction electrons to the local moment were obtained for both Fe and Cr atoms.

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