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Possibility of collinear magnetic order in frustrated free-standing Fe_2Cr_4 clusters

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Using the fully unconstrained version of the density-functional method SIESTA with the generalized gradient approximation for exchange and correlation, we compute the structures and magnetic configurations of the lowest-energy isomers of the free-standing cluster Fe_2Cr_4. The two most stable isomers of distorted octahedral geometry exhibit magnetic frustration but collinear magnetic order, in contrast to the behavior of extended Cr/Fe frustrated systems. Confinement effects and structural relaxation are shown to be the origin of this difference, which illustrates the importance of finite-size effects on magnetism.

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The coupling of different magnetic materials across an interface has attracted much attention in recent years, not least because of the importance of interlayer exchange coupling[1,2] and giant magnetoresistance.[3,4] Among the most complex and most extensively studied systems of this kind are ultrathin layers of antiferromagnetic (AFM) metals on ferromagnetic (FM) substrates, such as Mn/Fe(001) and Cr/Fe(001) (see Ref. 5 and references cited therein). In spite of the common AFM character of bulk Mn and Cr, the magnetic properties of Mn/Fe(001) and Cr/Fe(001) systems are different in many respects. According to a recent theoretical study using the *ab initio* all-electron tight-binding linear muffin-tin orbital method (TB-LMTO),[6] the most stable configuration of Mn-coated Fe(001) systems, among several with small energy differences, exhibits strong FM coupling between Mn and Fe at the interface, which together with the AFM tendency of Mn leads to an arrangement in which the coupling within each Mn layer is FM and the coupling between adjacent Mn layers is AFM.[7] By contrast, a TB-LMTO study of Cr-coated Fe(001) systems found that the only stable configuration has AFM coupling at the Cr/Fe interface, although the Cr film exhibits a layered AFM arrangement similar to that of the Mn film in Mn/Fe(001).[8] Studies of Mn and Cr films on a stepped Fe(001) surface, performed using a TB-LMTO-parametrized self-consistent real-space tight-binding model without imposing collinear (CL) spin alignment, have also shown striking differences between these two AFM metals: although in both cases there is an extended noncollinear (NCL) magnetic-moment distribution that arises from the magnetic frustration associated with the structural defect, only Cr shows large reductions in magnetic-moment amplitudes with values close to zero at some positions.[8,9]

To gain insight into the behavior of AFM/FM systems at the cluster level, we recently investigated[10] the structural and magnetic properties of the cluster Fe_2Mn_4 using the fully unconstrained option of the density-functional computation package SIESTA,[11] which has been applied to a wide variety of systems including several magnetic nanostructures[12] and, in its standard version,[13] uses the local spin-density approximation (LSDA) for exchange and correlation.[14] Our calculations predicted that the most stable isomer of Fe_2Mn_4 has distorted octahedral geometry and CL magnetic moments: the Fe atoms are adjacent and couple ferromagnetically both to each other and to their nearest two Mn neighbors, to which the other two Mn atoms couple antiferromagnetically. Thus, according to SIESTA/LSDA, ground-state Fe_2Mn_4 is magnetically reminiscent of the Mn-coated Fe(001) systems studied by Martínez *et al.*[7] However, a fully unconstrained SIESTA study of Fe_2Mn_4 using the generalized gradient approximation (GGA) for exchange and correlation (see Refs. 15–17) predicts that the most stable isomer has distorted octahedral geometry and NCL magnetic order.[18] Clarification of whether this cluster really behaves like the extended Mn/Fe(001) system is thus hindered by the circumstance that, as in the case of pure Mn clusters,[19] magnetic predictions for Fe-Mn clusters appear to depend critically on the approximation used for the exchange and correlation potential.

Whether a free-standing cluster behaves magnetically like a related extended system depends on the fundamental issue of how confinement affects magnetic noncollinearity. In view of the above-noted difficulty in using Fe-Mn systems to investigate this issue, we decided to study an Fe-Cr cluster, Fe_2Cr_4, and compare its behavior with that of the Cr/Fe(001) system described above. Here we report our results. Like Longo *et al.*,[18] we used SIESTA/GGA with NCL spin arrangements. Although in practice, for some metals (such as Pd), LSDA results are sometimes very similar to those obtained with the GGA (Ref. 20) and sometimes even better than them,[20,21] gradient corrections have been found to be necessary for systems such as bulk Fe (Refs. 22–24) and Cr,[25,26] and Cr clusters.[27] The GGA, therefore, seems likely to be the more accurate approximation for Fe-Cr clusters.

Core electrons were represented by nonlocal norm-conserving pseudopotentials[28] factorized in the Kleinman–Bylander form.[29] The Fe pseudopotential was generated using the valence configuration $3d^7 4s^1$ because, although that of the free atom in its ground state is $3d^6 4s^2$, studies of Fe nanostructures suggest that in these systems the former configuration predominates.[30,31] The reference valence configuration for Cr, including semicore electrons, was $3p^6 3d^5 4s^1$. The pseudopotential radii employed in our calculations for s, p, d, and f orbitals were all 2.00 a.u. for Fe, and for Cr were

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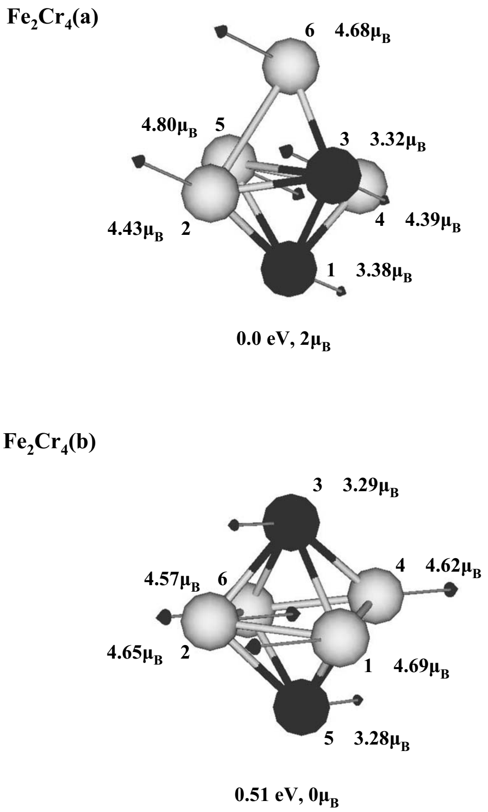

FIG. 1. Lowest-energy isomers of Fe_2Cr_4 with their relative energies, and total and local spin magnetic moments. Arrows indicate the direction and magnitude of the spin polarization at each atomic site. Numbers on atoms are used to refer to these atoms in Table I and in the text.

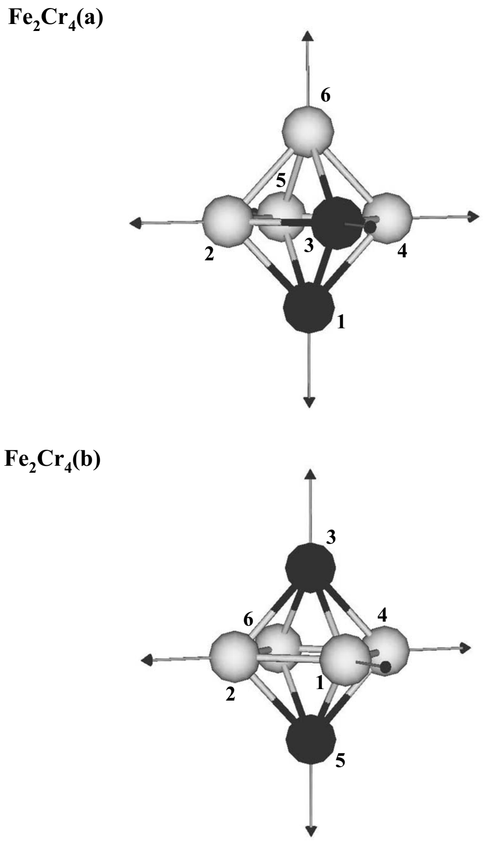

FIG. 2. Starting configurations of Fe_2Cr_4, leading, after relaxation, to the isomers shown in Fig. 1.

2.58, 1.40, 1.50, and 1.09 a.u., respectively. Valence states were described using triple-ζ doubly polarized basis sets. The cluster was allowed to relax without any symmetry or spin constraints until interatomic forces were smaller than 0.001 eV/Å. The quality of the Fe and Cr pseudopotentials is supported by the good agreement between the calculated dimer bond lengths, 2.01 and 1.8 Å, respectively, and the corresponding experimental values, 2.02 and 1.7 Å (Ref. 32). Spin-orbit interactions were ignored because they are known to have little influence on the magnetic properties of 3d transition-metal clusters.[33,34]

Fe_2Cr_4 isomers were sought by relaxation of a number of different starting geometries and magnetic configurations. The two isomers of lowest energy (Fig. 1) were obtained from the NCL configurations shown in Fig. 2. Interatomic distances are listed in Table I. Both isomers have distorted octahedral geometry and CL magnetic order. In the more stable isomer, $Fe_2Cr_4(a)$, the two Fe atoms are adjacent and couple ferromagnetically to each other while the coupling between nearest-neighbor Cr atoms within the Cr subcluster is AFM. Magnetic frustration in this isomer is apparent in the FM couplings Fe(1)-Cr(5), Cr(6)-Cr(2), and Cr(6)-Cr(4). In the less stable isomer, $Fe_2Cr_4(b)$, in which the two Fe atoms are too far apart for direct magnetic coupling, there is also magnetic frustration: each Fe atom couples antiferromagnetically to two of its Cr neighbors but ferromagnetically to the other two. Neither isomer shows any tendency to form dimers in the Cr subcluster as pure clusters of $3d^5 4s^1$ Cr atoms do as a consequence of the strong interactions between their half-filled 3d orbitals.[35]

It should be noted that the magnetic frustration in $Fe_2Cr_4(a)$ and $Fe_2Cr_4(b)$ coexists with a CL spin distribution, whereas extended frustrated Fe/Cr systems adopt an NCL configuration in the proximity of the structural[9] or compositional[36] defect that gives rise to frustration. Assuming that $Fe_2Cr_4(a)$ corresponds to the ground state (which we naturally cannot guarantee), this difference, which illustrates the importance of finite-size effects in magnetism, can be understood as follows. In extended systems, the manifestation of frustration and its associated energy can be widely distributed: noncollinearity can take the form of small angular differences between nearest neighbors over a large region.[8,9] By contrast, the confined nature of finite systems means that in NCL arrangements the angular differences between nearest-neighbor magnetic moments must be larger, and therefore require a large energy input. The same cause underlies the nonzero width of domain walls in extended systems: the energy necessary for numerous small relative rotations of the spin magnetic moments of successively adjacent atoms in a wide domain wall is less than what is required for the same total relative rotation to be set up between two adjacent sites (i.e., for the spin magnetic moment to flip between one site and the next).

Unlike the distribution of frustration energy, its reduction by structural relaxation can occur more easily in free-

TABLE I. Interatomic distances (in Å) in the two lowest-energy isomers of Fe_2Cr_4 (atom numbering as in Fig. 1).

	R_{12}	R_{13}	R_{14}	R_{15}	R_{16}	R_{23}	R_{24}	R_{25}	R_{26}	R_{34}	R_{35}	R_{36}	R_{45}	R_{46}	R_{56}
$Fe_2Cr_4(a)$	2.76	2.35	2.72	2.81	4.21	2.58	4.38	2.87	3.35	2.56	3.07	2.52	2.84	3.39	2.77
$Fe_2Cr_4(b)$	2.82	2.93	2.80	2.71	3.94	2.65	3.91	2.84	2.83	2.65	3.86	2.83	2.86	2.73	2.58

standing clusters than in supported extended systems, in which the atoms are essentially constrained to occupy the points of a pre-established lattice. That this has occurred in the present study is evidenced by the fact that atom pairs with frustrated pairwise coupling (e.g., FM instead of the expected AFM) are considerably farther apart than nonfrustrated pairs: in $Fe_2Cr_4(a)$, for example, R_{15} is larger than R_{12}, R_{14}, and R_{13}; and R_{62} and R_{64} are also larger than R_{65} and R_{63} (see Table I). Increasing the distance between a frustrated pair of atoms is an efficient way to reduce the energy associated with frustration and results in the average interatomic distance being larger in these clusters than in bulk Cr and Fe (whereas nonfrustrated free-standing clusters are generally more compact than the corresponding bulk metals). It seems likely that the high confinement-related energy cost of NCL configurations in small free-standing clusters and the relative ease of their structural relaxation together lead to free-standing Fe-Cr clusters, in general, having a stronger tendency to adopt CL configurations than their frustrated extended counterparts.[9]

To sum up, our fully unconstrained SIESTA/GGA calculations predict that the two lowest-energy isomers of Fe_2Cr_4 both exhibit distorted octahedral geometry, magnetic frustration, and CL magnetic order, in contrast to the behavior of frustrated extended Cr/Fe systems.[9] This is due to the magnetic frustration in these nanostructures being released through structural relaxation rather than through the development of NCL magnetic arrangements.

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