

**Noncollinear magnetism of Cr clusters on Fe surfaces**

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(Received 28 March 2006; revised manuscript received 26 June 2006; published 6 September 2006)

The magnetic properties of small Cr clusters on Fe surfaces have been investigated using a self-consistent noncollinear *spd* tight-binding method, parametrized through *ab initio* tight-binding linear muffin-tin orbital results. A competition between antiferromagnetic coupling within the cluster and antiferromagnetic coupling with the Fe surface has been found, leading to noncollinear magnetic arrangements for some configurations. The origin of this behavior is discussed in terms of magnetic frustration and with the aid of Heisenberg exchange parameters, which have been extracted from the calculations.

DOI: [10.1103/PhysRevB.74.094403](https://doi.org/10.1103/PhysRevB.74.094403)

PACS number(s): 75.75.+a, 73.22.-f, 75.10.Lp

**I. INTRODUCTION**

The study of supported nanostructures has attracted a lot of attention from the scientific community in the last few years. These systems are very interesting not only because of their technological applications, but also due to their intriguing electronic properties. These properties are in the limit between those of low dimensionality systems and those of bulk, and they are the result of the interplay between the intrinsic properties of the nanostructure and the properties of the substrate. So in order to elucidate them, many factors have to be taken into account, like the composition, size, and shape of the nanostructure; the substrate material and its crystallographic orientation; the hybridization of the electronic states of the nanosystem with the substrate, etc. Therefore the study of these systems is very challenging both for experimentalists and theoreticians.

In this work we will study magnetic nanostructures, focusing on the magnetic properties. Supported magnetic nanostructures are of special interest due to their potential application in high-density magnetic storage devices. In low-dimensionality systems, like free or supported nanoclusters, the magnetic properties are different to those of bulk. For example, due to the reduction of the average coordination the local magnetic moments are enhanced.<sup>1-6</sup> At the same time, the hybridization with the substrate may decrease the magnetic moment, leading to an equilibrium situation between the enhancement due to the loss of coordination and the hybridization with the substrate.<sup>7</sup> On the other hand, if the substrate is magnetic, the magnetic coupling between substrate and nanostructure also plays an important role. For example, if this coupling is antiferromagnetic (AF), frustration can appear and the final state may very well be noncollinear.

Experimentally, the supported nanostructures have the advantage of being directly accessible and the interest of their magnetic properties has favored the development of several techniques. One of them is the spin-polarized scanning tunneling microscopy (SP-STM),<sup>8</sup> which allows for having magnetic sensitive images with very high resolution. Another powerful technique is the x-ray magnetic circular dichroism (XMCD),<sup>1</sup> which determines the magnetic moment of small supported clusters. These techniques and others have opened the possibility of confirming many theoretical predictions and can be used in the future to study a great variety of supported nanostructures.

In particular, in this work we will study the magnetic properties of small Cr clusters on Fe surfaces. The Fe-Cr interface belongs to the group of systems mentioned above, i.e., systems with AF coupling where a noncollinear magnetic order may appear due to competition. One example is a recent work in Cr films supported on a stepped Fe(001) surface,<sup>9</sup> where it is shown how a magnetic frustration caused by a structural defect leads to a noncollinear situation. In the case of small Cr clusters the scenario is different. Several *ab initio* calculations<sup>2-4</sup> have shown that these clusters show noncollinear arrangements in the free-standing situation. In this case the reason is the AF coupling within the cluster, which may lead to frustration depending on the geometrical configuration. In the frustrated cases a noncollinear arrangement appears as the most stable state. In the systems studied here, it will be a competition between the AF coupling (i) within the cluster and (ii) between Fe and Cr, which opens a number of possibilities that will be studied in the present work.

**II. THEORETICAL METHOD AND COMPUTATIONAL DETAILS**

The spin-polarized electronic structures were determined by self-consistently solving a tight-binding (TB) Hamiltonian for the *s*, *p*, and *d* valence electrons in a mean-field approximation. The Hamiltonian can be split into a band term and an exchange term. The band term contains both the nondiagonal matrix elements (hopping integrals between orbitals of different sites, which are assumed to be spin independent) and the spin-independent part of the diagonal matrix elements. The exchange term describes the magnetic part, in which the direction of the local magnetic moments is not restricted to a global spin-quantization axis. To solve the Hamiltonian, the local densities of states are calculated by using the recursion method<sup>10</sup> in the real space. Our model provides the partial densities of states projected on an arbitrary local quantization axis (instead of a global one) through a rotation of the initial recursion vector in the spin space. Once the local densities of states are determined, we calculate the local electronic occupations and local magnetic moments at each site by integrating them up to the Fermi level with the global charge neutrality condition. More details about the model and the numerical procedure can be found

elsewhere.<sup>9</sup> The choice of a TB model to face this problem and not an *ab initio* scheme is justified by the computational demands for this problem. Typically, we are dealing with systems without symmetry in any direction, which severely hampers the efficiency of most *ab initio* methods. Moreover, the possibility of a noncollinear configuration typically increases the time required for the convergence of the solution by one order of magnitude, since the convergence of the angular components is extremely slow. The method used in this paper allows for keeping the computational demands at an acceptable level for reasonable sizes of clusters, while simultaneously keeping a good accuracy, as have been shown in recent works.<sup>5,6</sup>

We have considered the Cr clusters to be supported on two different crystallographic orientations: bcc and fcc. In the first one, the Cr clusters have been deposited on a Fe(001) surface. In the fcc situation, the Cr clusters have been deposited on three Fe monolayers supported on a Cu(001) surface. The pseudomorphic growth of Fe on Cu(001) has been proposed to stabilize the fcc phase of Fe, although recent papers have challenged this possibility.<sup>11-13</sup> In this work we are interested in the theoretical behavior of the magnetic properties of the clusters, especially under which conditions a noncollinear behavior may appear. Thus we have chosen to keep the picture as simple as possible. In that sense the proposed fcc system is the simplest we could make up to compare with the bcc situation. Actually, a larger number of Fe layers on Cu(001) or a pure Fe(001) fcc surface would have been more complicated due to the intrinsic nature of fcc Fe. So we have considered a situation where *ab initio* calculations<sup>14</sup> predict a ferromagnetic (FM) configuration for Fe, but with a different environment than the usual bcc. For the sake of simplicity, we have also used unrelaxed positions in both situations, proposing possible cluster geometries following a pseudomorphic growth.

The parameters of the TB model have been determined as follows. For the bcc configuration we have used the same parametrization as in Ref. 9. For the fcc environment, the homonuclear hoppings were obtained by fitting the model to TB linear muffin-tin orbital (TB-LMTO) (Ref. 15) results for a related system, in this case one Cr monolayer over three Fe monolayers deposited on Cu(001). This fit allows both the influence of the surface and possible hybridization to be taken implicitly into account. In fitting the TB model to the TB-LMTO data, the TB hopping parameters were obtained by the method described by Andersen and Jepsen for bulk solids,<sup>15,16</sup> here adapted for a semi-infinite system. The direct Coulomb integrals have been taken from a previous work<sup>17</sup> and the exchange integrals have been taken as in the bcc situation.

As indicated before, the cluster geometries have been chosen to follow a pseudomorphic growth. This assumption is reasonable in the case of supported clusters, and has been used by other groups,<sup>6,18</sup> and confirmed in cases where a geometry optimization was performed.<sup>5</sup> For some sizes, several cluster shapes have been considered. Although no relaxation has been taken into account, the influence of both relaxation and different cluster shape will be discussed. All Cr atoms in the cluster and the surrounding Fe atoms up to fourth neighbors have been considered as inequivalent sites

and they have been included in the self-consistent calculation. We have tested that the results do not change by increasing the number of active Fe neighbors.

### III. RESULTS AND DISCUSSION

Before showing the results, let us analyze both bcc and fcc situations. In the bcc case, first nearest neighbors of Cr atoms will always be Fe atoms. Second nearest neighbors can be Cr atoms, so the closest distance between Cr atoms is equal to the bcc Fe lattice parameter (2.87 Å). In the fcc case, Cr atoms can have Cr nearest neighbors, so the closest Cr-Cr distance is the nearest-neighbors distance in fcc Cu (2.55 Å). Therefore a stronger AF coupling within the cluster is expected for the fcc case. For the Fe-Cr coupling a similar behavior is expected for bcc and fcc situations, since in both cases each Cr atom has four Fe first nearest neighbors at similar distance (2.49 Å for bcc and 2.55 Å for fcc).

The first case to analyze is the dimer. For the bcc surface we have found that the only stable solution is a collinear configuration with both Cr atoms coupled antiferromagnetically with Fe and showing an almost saturated moment ( $3.78\mu_B$ ). On the other hand, in the fcc case we have found that the most stable situation is a noncollinear configuration where the magnetic moments of Cr atoms are  $3.82\mu_B$  and they form an angle of  $84^\circ$  with each other. This behavior can be analyzed by fitting to a Heisenberg-like model. In order to do so, we have performed some additional calculations in which the angle between the atoms of the dimer was fixed. This data has been used to fit the equation

$$\Delta E(\theta) = -J_{\text{Fe-Cr}}[\cos(\pi - \theta/2) + 1] - J_{\text{Cr-Cr}}[\cos \theta - 1],$$

where  $\theta$  is the angle between the magnetic moments of dimer atoms. The first term represents the bilinear exchange between the Cr dimer and the Fe surface, whereas the second term represents the bilinear exchange between Cr atoms in the dimer. From this fit we get  $J_{\text{Fe-Cr}} = -0.79$  eV and  $J_{\text{Cr-Cr}} = -0.11$  eV for bcc; and  $J_{\text{Fe-Cr}} = -0.72$  eV and  $J_{\text{Cr-Cr}} = -0.11$  eV for fcc. As expected, all the exchange parameters are negative, which means that all couplings are AF. The values for  $J_{\text{Fe-Cr}}$  are similar for both structures, but a little bit larger for bcc because of the slightly closer distance between Fe and Cr atoms. For  $J_{\text{Cr-Cr}}$ , the value is more than twice larger in fcc than in bcc, and the condition for noncollinearity ( $|J_{\text{Fe-Cr}}| < 4|J_{\text{Cr-Cr}}|$ ) is fulfilled.<sup>19</sup> Therefore the results agree with our previous geometrical discussion: whereas the interaction between Fe and Cr is similar in both situations, the interaction between the Cr atoms is much more important in the fcc case and leads to a noncollinear configuration.

For the bcc orientation we have studied planar Cr clusters up to ten atoms with several shapes. Following the behavior for the dimer, the smaller clusters (up to four atoms) have collinear magnetic moments with a AF coupling to Fe. In Fig. 1 the shapes and magnetic moments are shown, as well as the average magnetic moment of the cluster. As for the dimer, the magnetic moments are closer to saturation and their behavior can be related with the local coordination, i.e., the atom with more neighbors have a slightly lower magnetic

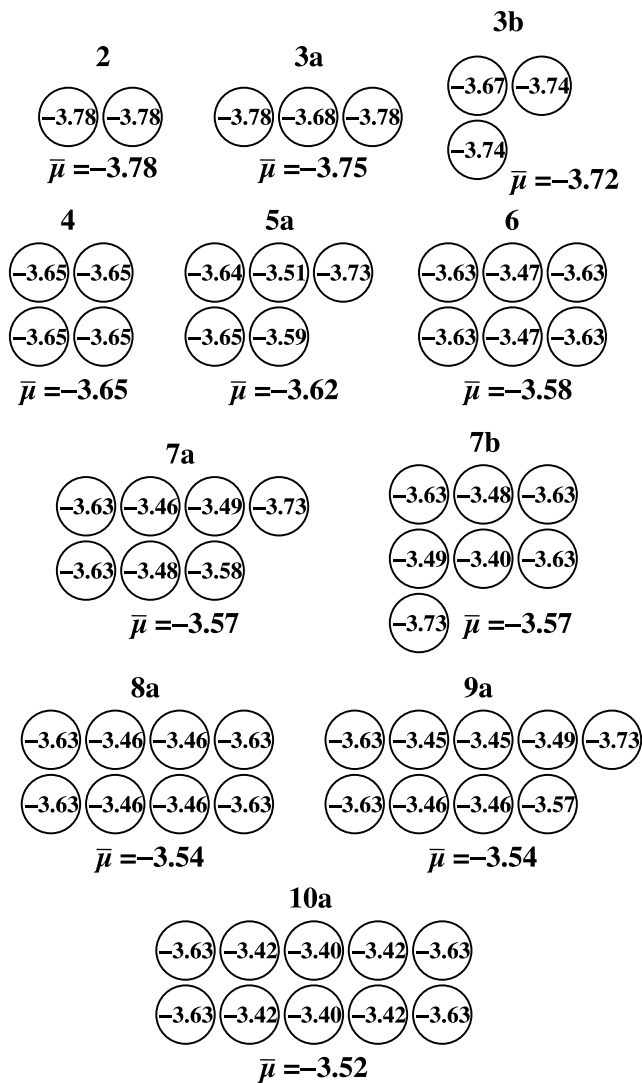


FIG. 1. Top view of Cr clusters on Fe(001) in the bcc orientation for which the most stable solution is collinear. Magnetic moments (in  $\mu_B$ ) of all sites and average magnetic moment are given for each size and shape. The minus sign means AF coupling with Fe.

moment. However, for most of the clusters several collinear configurations can be converged, reflecting the competition between the coupling within the cluster and the coupling with the substrate. In all cases, the most stable collinear configuration is the one with all Cr having their magnetic moments parallel to each other and antiparallel to the Fe atoms. The existence of several collinear configurations is usually an indication of a possible noncollinear arrangement. Actually, for clusters bigger than five atoms a noncollinear configuration can be obtained, although only for some shapes it is slightly more stable than the collinear case. In Fig. 1 we show the clusters where the collinear structure is more stable, and in Fig. 2 we show the ones which present a noncollinear ground state. For the collinear clusters, it can be observed how the magnetic moment decreases as increasing the average coordination number of the cluster. For the noncollinear clusters, looking at the shapes it is possible to distinguish a pattern which makes the noncollinear configuration more stable. This pattern is illustrated with the cluster 5b, where

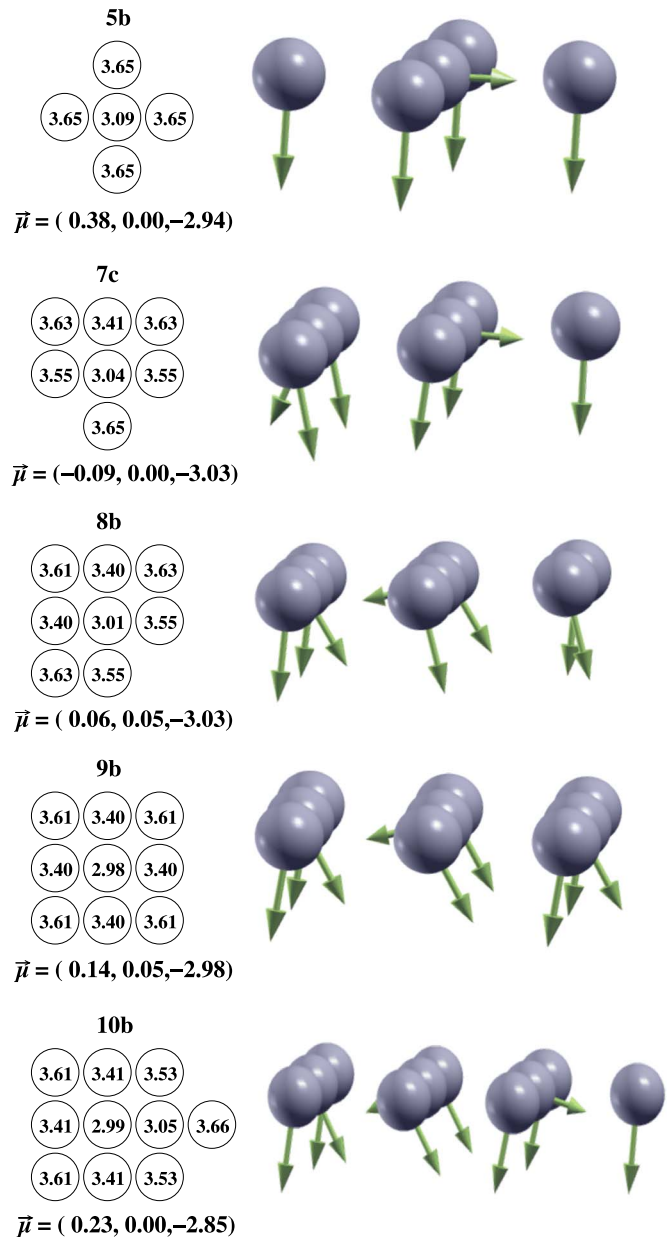


FIG. 2. (Color online) (Left panel) Top view of Cr clusters on Fe(001) in the bcc orientation for which the most stable solution is noncollinear. The modulus of the magnetic moment (in  $\mu_B$ ) for every site and three components of the average magnetic moment are given for each cluster. (Right panel) Perspective view of the noncollinear solution.

the central atom has four Cr atoms as second nearest neighbors. So we can say that the cause of the noncollinearity is related to this kind of atoms, where the tendency to an AF coupling within the cluster is more important due to the higher number of Cr neighbors. The magnetic moment of these atoms is tilted to form an angle with Fe closer to  $90^\circ$ , as a result of the competing situation. The four closer Cr atoms tilt as well, trying to keep the AF coupling. Due to this effect, the average magnetic moment of the whole cluster is pointing to form an almost perfect AF coupling with Fe, with a small moment in  $x$  or  $y$  directions. Although it has not been shown here, the magnetic moments of closer Fe atoms are

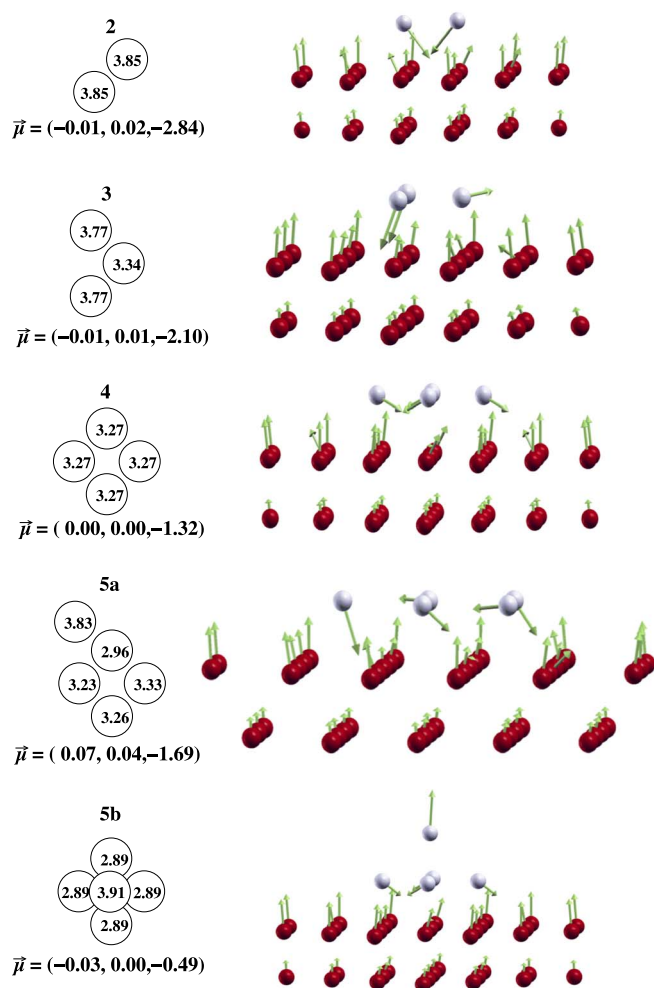


FIG. 3. (Color online) (Left panel) As in left panel of Fig. 2 but for the fcc orientation. (Right panel) Perspective view of the noncollinear solution. In this case Cr (light) and the closest Fe (dark) atoms are shown.

also slightly perturbed, with small components in-plane of at most  $0.3\mu_B$ .

In general, it can be said that in the bcc environment there is a competition between collinear and noncollinear configurations for clusters bigger than four atoms. This is reflected in the existence of several collinear configurations and in the small energy difference (a few meV) between the most stable of them and the noncollinear configuration. In our calculations, we predict that the latter one is favorable when the AF coupling within the cluster is strong enough. This condition is fulfilled when the pattern illustrated with the cluster 5b appears. Therefore the possibility of having a noncollinear configuration depends on the shape of the cluster and possibly in other details, like the relaxation of the atomic positions. However, the important point is the presence of a competition between collinear and noncollinear solutions.

For the fcc orientation the situation is different. In Fig. 3 the most stable solution for clusters between 2 and 5 atoms is shown. For all these sizes and shapes the most stable solution is a noncollinear configuration. As we have seen for the dimer, the tendency to a AF configuration within the cluster

is higher in this case than for the bcc one and therefore even for the smallest sizes the noncollinear solution is preferred. The only exception we have seen, not shown here, is a five-atom cluster with the same geometry of the 5b bcc configuration. In this case, due to the favorable symmetry, the AF coupling within the cluster is strong enough to make the collinear  $c2 \times 2$  configuration (the central Cr atom pointing opposite to the other Cr atoms) more stable than the noncollinear solution that we have found. Actually, for the five-atom shape shown in Fig. 3 in the most stable collinear solution one of the Cr atoms is antiferromagnetically coupled to the others. The behavior of the average magnetic moment of the cluster is similar to the found in the bcc case. However, now the resulting magnetic moment in the  $z$  direction is much smaller, due to the stronger “noncollinearity,” that is reflected in bigger  $x$  and  $y$  components for the atoms. These components cancel each other to a large extent, and finally we obtain the shown average magnetic moment. The case of pyramidal configuration of the five-atom cluster (5b in Fig. 3) is specially interesting. The obtained solution is essentially the one of the four-atom cluster with an atom on top of it which is antiferromagnetically coupled to the resultant of the four atoms below it. As a result, the average magnetic moment of the cluster is remarkably small,  $0.49\mu_B$ . Another point to remark is that for this orientation the closest Fe atoms are much more perturbed than in the bcc case. As can be seen in Fig. 3, some of the Fe atoms which are first neighbors of the Cr ones are tilted more than  $45^\circ$  which respect to the original position. This remarkable perturbation in Fe is understood by taking into account the properties of fcc Fe, which bulk ground state is noncollinear. Therefore the deviation from the collinear situation is likely to cost less energy in this case than in bcc Fe, where the ground state is FM. On the other hand, the relaxation of Fe is very important to stabilize the noncollinear solution. If the Fe magnetic moments are fixed to keep a FM coupling with no  $x$  and  $y$  components, the noncollinear solution is then less stable than the collinear one.

Comparing to the bcc orientation, in the fcc one the energy difference between collinear and noncollinear situations is much bigger (hundreds of meV), and it can be concluded that, except in cases where the geometry favours a  $c2 \times 2$  collinear configuration, the Cr clusters will have a noncollinear distribution of magnetic moments.

As mentioned before, we have not performed any structural optimization or molecular dynamics calculation to study the most stable geometries of the clusters or how much the distances relax. Both for the bcc and fcc situations, we have shown that the shape of the clusters is important to see if a collinear or a noncollinear situation is the most stable. A molecular dynamics calculation should be performed to determine which is the preferred shape and therefore if the cluster is noncollinear in its ground state. The relaxation of atomic distances can also be important since it alters the strengths of the competing couplings. In order to estimate these effects, we have performed several test calculations with the distances varied with up to 5%. For example, for the 8b cluster in the bcc orientation the average magnetic moment of the relaxed cluster is  $(-0.04, 0.00, -3.08)$ . The local spin orientations are the same within a few degrees. The

same holds for the  $5a$  cluster of the fcc orientation, where the average magnetic moment is  $(0.09, 0.05, -1.70)$  and the local spin configuration is also very close. After these tests we can conclude that the overall picture remains valid under realistic relaxations.

#### IV. CONCLUSIONS

By means of a self-consistent noncollinear TB method we have studied the magnetic properties of small Cr clusters in a Fe(001) bcc and fcc surfaces. We have seen that in both situations there is a competition between AF coupling within the cluster and AF coupling with the underlying Fe. In the bcc orientation this competition leads to a noncollinear situation as the most stable one only for some shapes in which a particular pattern appears. In the fcc case the tendency to the noncollinearity is stronger and the clusters are noncollinear in almost all cases. For this orientation we have shown that the noncollinear perturbation of Fe is very important to sta-

bilize the noncollinear solution. In both cases the average magnetic moment of the clusters is close to a perfect AF coupling with Fe.

Some questions are still unsolved for these systems. As we have seen, the shape is crucial to determine if the ground state for a given cluster size is noncollinear. So a molecular dynamics should be performed to determine the shape and relaxation of the cluster. Other aspects should also be considered, like the possibility of having three-dimensional structures or the intermixing of Fe and Cr in the cluster. A study on these topics is being performed and will be reported in the future.

#### ACKNOWLEDGMENTS

We are grateful to support from the Swedish Research Council and the Swedish Foundation for Strategic Research. We also thank the Swedish National Infrastructure for Computing (SNIC) for support.

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<sup>19</sup>The expression for the noncollinearity condition is calculated by imposing the existence of a minimum for  $\Delta E(\theta)$  different than 0 or  $\pi$ .