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Non-collinear Magnetic Moment of Linear-chain Fe Clusters

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Magnetic moments of linear-chain clusters, Fe_5 and Fe_7, are calculated by the non-collinear local spin-density functional method. For both the clusters with a certain interatomic distance, the magnetic moment at each atomic site gradually tilts from the center to the ends, that is, the magnetic moments has a radial arrangement. This non-collinear arrangement is understood as the competition between the ferromagnetic interaction for the fist nearest neighbors and the antiferromagnetic interaction for the second nearest neighbors.

Key words: non-collinear, density functional, magnetic moment, cluster

1. INTRODUCTION

Recent progress of nano-technology has achieved the ability to construct atomically engineered materials such as the nano-wire of atom-size thickness.[1] These materials have very interesting quantized features. For example, the atom-size wire has a conductance quantized in units of $2e^2/h$ for noble metal materials[2] and e^2/h for transition metal materials as the wires are stretched.[3,4]

The magnetic property in nano-wire of transition metal is also very interesting because of the low dimension and size effects, which lead to giant and frustrated magnetic moments. Morigaki *et al.* have revealed,[5] in their calculation with the Hubbard model, that the magnetic property changes from paramagnetic to ferromagnetic and vice versa as the wire is stretched. It is also have revealed, by the non-collinear local spin-density calculation, that the magnetic moment of the linear Fe_3 cluster has a non-collinear magnetic property, where the magnetic moments of the both end sites tilt almost perpendicularly to that of the center sites.[6,7] A spiral magnetic arrangement also observed in pentagonal bipyramid clusters, Fe_7, Mn_7 and Cr_7, where the magnetic moment along the basal five atomic sites rotates with the angle of 72° or 144°.[8]

In the present paper, we calculate the magnetic moments of linear Fe_5 and Fe_7 clusters by the non-collinear local spin-density functional approximation with discrete variational scheme (LSDA-DV), and discuss the non-collinear magnetic properties as the interatomic distances are changed. It is shown that the magnetic moments for both the clusters gradually tilt from the center to the ends, that is, the magnetic moments has a radial arrangement.

2. CALCULATIONS

Magnetic moments of the linear-chain clusters are calculated by the non-collinear LSDA-DV method, which is based on the non-collinear Kohn-Sham equation,[9]

$$\left\{\left(-\nabla^2 + v_0 + \bar{v}_{xc}\right)\boldsymbol{I} + \Delta v_{xc}\tilde{\boldsymbol{\sigma}}_z\right\}\begin{pmatrix}\Psi_i^\alpha\\ \Psi_i^\beta\end{pmatrix} = \varepsilon_i\begin{pmatrix}\Psi_i^\alpha\\ \Psi_i^\beta\end{pmatrix}. \quad (1)$$

Here, Ψ_i^σ is the one-electron orbital which generates the 2×2 spin-density matrix. v_0 is the electrostatic potential from nuclei and electrons. $\bar{v}_{xc}$ and Δv_{xc} are the spin-independent and spin-dependent terms of the exchange-correlation potentials, respectively; $\bar{v}_{xc} = (\delta E_{xc}/\delta\rho^1 + \delta E_{xc}/\delta\rho^2)/2$ and $\Delta v_{xc} = (\delta E_{xc}/\delta\rho^1 - \delta E_{xc}/\delta\rho^2)/2$. $\delta E_{xc}/\delta\rho^1$ and $\delta E_{xc}/\delta\rho^2$ are locally oriented exchange-correlation potentials obtained by the usual LSDA with the spin-densities $\rho^1(\boldsymbol{r})$ and $\rho^2(\boldsymbol{r})$, which are polarized to the local spin-axis at $\boldsymbol{r}$. $\boldsymbol{I}$ is the 2×2 unit matrix, and $\tilde{\boldsymbol{\sigma}}$ is the Pauli matrix unitarily transformed by the spin-rotation matrix at $\boldsymbol{r}$.

Eq.(1) is solved within the self-consistent charge scheme with the LCAO basis,

$$\begin{pmatrix}\Psi_k^\alpha\\ \Psi_k^\beta\end{pmatrix} = \sum_i c_{ki}\begin{pmatrix}d_{ki}^1\\ d_{ki}^2\end{pmatrix}\phi_i(\boldsymbol{r}), \quad (2)$$

where c_{ki}, d_{ki}^1 and d_{ki}^2 are complex coefficients. The $1s$-$4s$, $2p$-$4p$ and $3d$ atomic orbitals, which are numerically obtained from the potential around the each atom, are employed as the LCAO basis.

The initial condition of the absolute magnetic moment and the electronic configuration of each atom are taken as follows; 3.0 (μ_B), $3d_1^{5.0}3d_2^{2.0}$, $4s_1^{0.5}4s_2^{0.5}$,

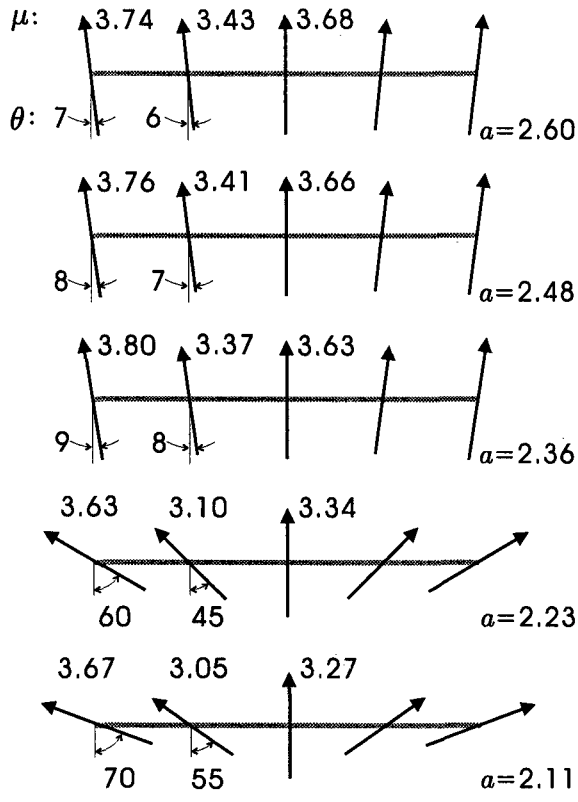

Figure 1: Non-collinear magnetic moment of the linear Fe_5 clusters for the interatomic dinstance, a = 2.11-2.60Å.

and $4p_1^{0.0}4p_2^{0.0}$, where the suffix 1 (2) means the up (down)-spin about the local axis. Some random directions are taken as the initial direction of the magnetic moment at each atomic site. In the present method, the relative direction of the magnetic moment for each atomic orbital is self-consistently obtained, but the absolute direction to the space cannot be determined. Therefore, in the following sections, the direction of the magnetic moment at the center atom of the linear-chains is fixed and the directions of the other atomic sites are shown as the relative directions to it.

The interatomic distance in a linear-chain cluster, a, is changed from 85% to 105% of the value in the bulk crystal, and the dependence of the non-collinearity on the interatomic distance is discussed.

3. RESULTS

3.1 Fe_5

Figure 1 shows the absolute value of magnetic moment, μ (μ_B/atom), and the direction, θ (degree), at each atomic site in the linear Fe_5 cluster for the interatomic distance, a = 2.11-2.60Å(85-105% of the value in bulk crystal). The length of the arrow also indicates the absolute value. The calculation shows that the magnetic moments for all the interatomic distances are in coplanar arrangement, that is, the magnetic moments of all the atomic sites orient on a plane. Thus, only the 2-dimensional direction is indicated in Fig.1.

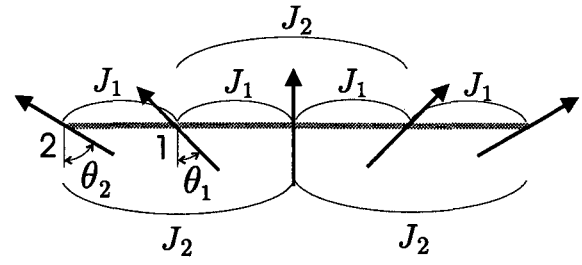

Figure 2: Schematic diagram of J_1-J_2 Heisenberg model for the linear Fe_5 cluster.

For larger interatomic distances, a = 2.36-2.60Å(95-105%), the magnetic moments align almost parallel to each other, although the magnetic moments at the outer atomic sites slightly tilt out (< 10°). The absolute magnetic moment is the largest at the ends of the chain and the smallest at the next to the ends. This behavior in the absolute value of magnetic moment is considered to be a kind of the Friedel oscillation, which is also observed on the layers from the surface to center in 3-dimensional transition-metal clusters.[10,11]

For smaller interatomic distances, a = 2.11-2.23Å(85-90%), the magnetic moments at the outer atomic sites tilt more with decreasing the interatomic distance, that is, the magnetic moment tilts oppositely from the center to both the ends. Oda *el al.* observed a similar magnetic arrangement in the linear Fe_3 cluster with 1.97Å of the interatomic distance, where the magnetic moment at the both ends tilt oppositely by 84° to that at the center site.[6] Such a non-collinear magnetic arrangement as these would be caused from the competition between the antiferromagnetic coupling for the second nearest neighbors and the ferromagnetic coupling for the nearest neighbors.

Here, we employ the J_1-J_2 Heisenberg model as a simple model to explain this non-collinearity, where J_1 is the ferromagnetic coupling between the nearest neighbors and J_2 the antiferromagnetic coupling between the second nearest neighbors. Figure 2 shows a schematic diagram of the this model for the Fe_5 cluster. Assuming the coplanar arrangement, the Hamiltonian H' in this model is expressed as

$$H' = -2J_1\{\cos\theta_1 + \cos(\theta_1 - \theta_2)\} + J_2\{\cos 2\theta_1 + 2\cos\theta_2\}. \quad (3)$$

$\theta_1(\theta_2)$ is the angle between the magnetic moments at the atomic sites 1(2) and the center.(See Fig.2.) Figure 3(a) shows θ_1 and θ_2 that give the minimum of Eq.(3) as function of the ratio, J_2/J_1. While $J_2/J_1 < 0.3$, $\theta_1 = \theta_2 = 0$, that is, the magnetic moment aligns parallel to each other. When $J_2/J_1 > 0.3$, θ_2 and θ_1 gradually increase with J_2/J_1, and θ_2 becomes over 90° at $J_2/J_1 = 0.48$. In comparison with the results by the LSDA-DV calculation in Fig.1, it is considered that the magnetic arrangement of the Fe_5 with the larger interatomic distance, a = 2.36-2.60Å, corresponds to that at $J_2/J_1 < 0.3$, and that the magnetic arrangement with

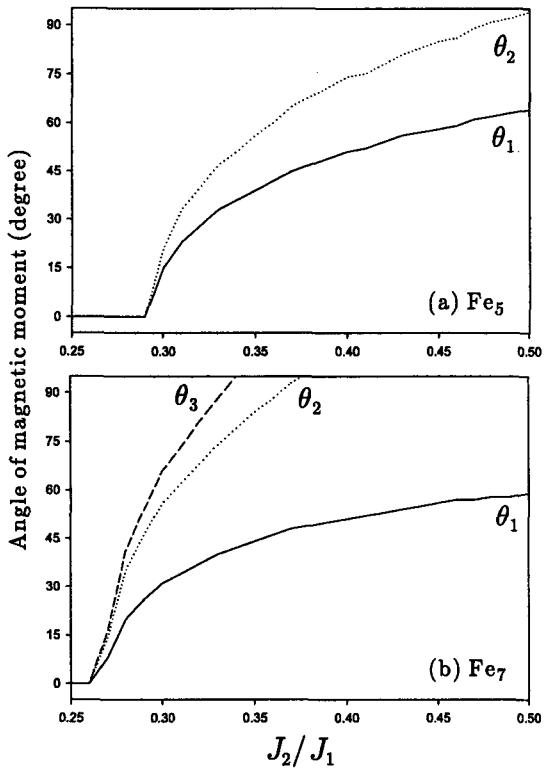

Figure 3: Angles between the magnetic moments at the minimum of H' as function of J_2/J_1, (a) for Fe_5 with Eq.(3) and (b) for Fe_7 with Eq.(4).

a = 2.11-2.23Å to that at $0.3 < J_2/J_1 < 0.5$.

3.2 Fe_7

Figure 4 shows the same as Fig.1 for the linear Fe_7 cluster. The calculation indicates that the magnetic arrangement of the Fe_7 cluster is also coplanar for all the interatomic distances. The absolute magnetic moment is the maximum at the end, the minimum at the next to the end, and the second minimum at the center, that is, the magnetic moment oscillates from the end to the center, similarly to that of the Fe_5 cluster.

For the larger interatomic distance, a = 2.48-2.60Å, the magnetic moments tilt by $\sim$ 65°, $\sim$ 55° and $\sim$ 20° at the atomic sites from the end to the center, respectively. For the smallest interatomic distance, a = 2.11Å, the magnetic moments at the two atomic sites to the ends (four sites for both sides) are almost perpendicular to that at the center. These magnetic arrangements also can be understood as the competitions between the antiferromagnetic interaction for the second neighbors and the ferromagnetic interaction for the first neighbors, which is simply described by the Heisenberg model similar to Eq.(3);

$$H' = -2J_1\{\cos\theta_1 + \cos(\theta_1 - \theta_2) + \cos(\theta_2 - \theta_3)\} + J_2\{\cos 2\theta_1 + 2\cos\theta_2 + 2\cos(\theta_1 - \theta_3)\}. \quad (4)$$

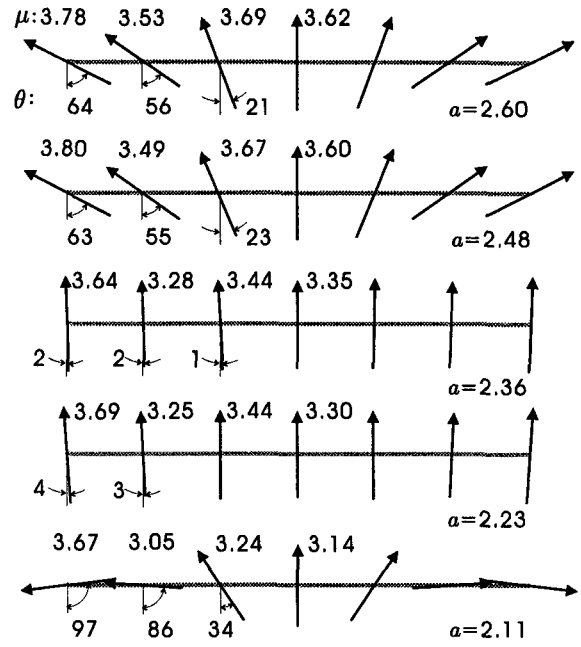

Figure 4: Non-collinear magnetic moment of the linear Fe_7 clusters for the interatomic dinstance, a = 2.11-2.60Å.

Here θ_1 and θ_2 are the same as those in Fig.2, and θ_3 is the angle of the magnetic moment at the end. Figure 3(b) shows the angles of the magnetic moments that gives the minimum of Eq.(4) as function of J_2/J_1. The magnetic moments begin to tilt from $J_2/J_1 = 0.27$, earlier than those for the Fe_5. The magnetic moments of the outer two sites (θ_2 and θ_3) rotate rapidly whereas that at the next to the center site, θ_1 rotates slowly and closes to the angle of 60° in this region of J_2/J_1. Comparing these angles with the results by the non-collinear calculation in Fig.4, it is found that the magnetic arrangement of the Fe_7 cluster with a = 2.48-2.60Å corresponds to that at $J_2/J_1 \sim 0.28$ and that with a = 2.11Å to that at $J_2/J_1 \sim 0.35$.

However, almost parallel magnetic alignment appears in the middle interatomic distance, a = 2.23-2.36Å, as shown in Fig.4. This magnetic behavior cannot be explained by the naive model of Eq.(4). How this parallel magnetic moment arises is not obvious so far, however, almost degenerate electronic levels cross over the highest occupied level during the middle interatomic distances, where the parallel magnetic alignment appears. The electronic states of these levels might play a role to emphasize the ferromagnetic interaction.[5]

4. CONCLUSION

Magnetic moments of linear Fe_5 and Fe_7 clusters are calculated by the non-collinear local spin-density functional method. The magnetic moments for both the clusters tilt gradually from the center to the ends for a certain interatomic distance. This non-collinearity in the magnetic property arises from the competition

between the ferromagnetic interaction for the nearest neighbors and the antiferromagnetic interaction for the second neighbors. A change of magnetic arrangement from non-collinear to parallel and vice versa also appears for the Fe_7 cluster as the interatomic distance varies. The non-collinear LSDA-DV method employed in the present calculation is so simple that it is applicable to larger systems. The calculation for the longer transition-metal chains will reveal the non-collinearity of the 1-dimensional system in detail.

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