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CALCULATION OF THE ELECTRONIC STRUCTURE AND MAGNETIC PROPERTIES OF IRON MICROCLUSTERS

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ABSTRACT. Calculations of a spin-polarized electronic structure and magnetic moment of small iron clusters within the framework of the local spin-density approach and the model "atom in jellium" have been presented. It is shown that the occupation of localized d-states of atoms in iron clusters changes nonmonotonically depending on the atom position in relation to the cluster surface as well as on the cluster size. The nonmonotonic change of the electronic structure results in the nonmonotonic size dependence of iron cluster magnetic properties.

1. INTRODUCTION

Recently the properties of small transition clusters have been studied intensively. With development of methods to produce clusters of controlled size it has become possible to perform experiments on their electron and magnetic properties. For example, the magnetic moment [1], chemisorption reactivity [2] and ionization potential [2] of such clusters have been measured.

Theoretical investigations of cluster physical properties are carried out actively too. A variety of theoretical models has been proposed for calculations of a cluster electronic structure. However, most precise models (such as the

self-consistent-field X_α -scattered wave method or some other methods) permit to obtain an electronic structure for clusters with low number of atoms. For large atomic aggregations these methods cannot be applied successfully, and simpler models are employed in this case. Thus, for study of electronic properties of sp-bonded metal clusters the jellium model is used, and it gives an excellent description of the various experimentally observed data.

In this work we have calculated an electronic structure and magnetic moment of spherical iron clusters containing up to 130 atoms within the framework of the model "atom in jellium". (Models of this type have been used in the investigation of, e.g., chemisorption on metallic surface, impurities in bulk metal and small clusters of simple metals, optical properties of pure metals.)

2. MODEL AND METHOD

In our calculations atoms of a cluster are mimiced by atoms embedded in the centre of spherical-finite jellium. The jellium sphere radius R is determined according to the position of the real atom in relation to the cluster surface: R defines the short out between the atom and the cluster surface.

The electronic structure of an atom embedded in spherical jellium is obtained using the self-consistent Kohn-Sham equations (in atomic Rydberg units):

$$[-\nabla^2 + V^S(r)] \phi_{nls}(\vec{r}) = E_{nls} \phi_{nls}(\vec{r}), \quad (1)$$

$$V^S(r) = -\frac{2Z}{r} + 2 \int \frac{n^-(\vec{r}') - n^+(\vec{r}')}{|\vec{r} - \vec{r}'|} d\vec{r}' + V_{x0}^S(r), \quad (2)$$

$$n^-(\vec{r}) = \sum_{nls}^{oco} |\phi_{nls}(\vec{r})|^2 \quad (3)$$

with the Vosko form of the local spin-polarized exchange-correlation potential $V_{x0}^S(r)$. Here the spins is \uparrow, \downarrow ; Z is the central nuclear charge. The rigid positive charge distribution of the jellium background is given by

$$n^+(r) = n_0^+ \vartheta(R-r) \vartheta(r-r_c), \quad (4)$$

where $\vartheta(x)$ is the unit step function, R and r_0 being, respectively, the outer and inner radii of the positive background sphere; n_0^+ is taken to be the same as the mean valence electron density of the corresponding bulk metal:

$$n_0^+ = \frac{3 N}{4\pi (R^3 - r_0^3)}, \quad (5)$$

$$R = (N/N_a + 1)^{1/3} r_0, \quad (6)$$

r_0 is the Wigner-Seitz radius, N is the number of electrons in the jellium sphere, and N_a is the number of valence electrons in an atom of the cluster. We have employed for Fe $r_0 = 2.67$ a.u., $N_a = 2$.

The electron configuration of ground state of "atom in jellium" was determined from following reasoning. Rules of energy level occupation separately in jellium (in a spherical potential well) and in a free atom are known. Clearly, insertion of an atom in the jellium sphere centre does not change the atom and jellium field symmetry, and, consequently, the symmetry of their electron states is not changed, too. It was supposed therefore that the number of electron states with the same symmetry in the jellium cluster with the central atom is equal to the sum of such symmetry states of the jellium cluster and atom. The order of the energy level is obtained by solving the spin-polarized self-consistent Kohn-Sham equation (1-3) with the angular l and principal n quantum numbers. The total energy of the Fe atom in the jellium cluster is computed for various occupation numbers of the upper levels. As the ground state we have chosen the electron configuration with the lowest total energy.

It has been obtained that the five lowest energy levels of "atom Fe in jellium" are identical with those of an iron core, the rest of them are similar to the energy spectrum of a spherical potential well. This order is broken by the localized d -state in the upper part of the occupied energy region.

3. RESULTS

The electronic structure of iron atom embedded in the jellium sphere centre has been calculated as a function of the jellium size. It was found that the electronic structure of "atom Fe in jellium" alters periodically with the increase of the jellium sphere radius (or of the number of electrons in the

TABLE 1. The electron configurations of an iron atom embedded in jellium spheres containing from 10 to 60 electrons

N	majority spin	minority spin
	$1s^1 2s^1 1p^3 3s^1 2p^3 4s^1 3p^3 1d^5 \dots$	$1s^1 2s^1 1p^3 3s^1 2p^3 4s^1 3p^3 1d^5 \dots$
10	$\dots 2d^0$	$\dots 2d^0$
12	$\dots 2d^2$	$\dots 2d^0$
16	$\dots 2d^5 5s^1$	$\dots 2d^0 5s^0$
32	$\dots 2d^5 5s^1 1f^7$	$\dots 5s^1 1f^7 2d^1$
50	$\dots 5s^1 1f^7 4p^3 2d^5 1g^9$	$\dots 5s^1 1f^7 4p^3 2d^4 1g^0$
54	$\dots 5s^1 1f^7 4p^3 2d^5 1g^9$	$\dots 5s^1 1f^7 4p^3 2d^5 1g^3$
	$\dots 5s^1 1f^7 4p^3 2d^5 1g^9 \dots$	$\dots 5s^1 1f^7 4p^3 2d^5 1g^9 \dots$
60	$\dots 3d^0$	$\dots 3d^0$

jellium N according to (6)). Each period starts when the new empty d-level appears and is completed by its full occupation (see Table 1). The boundaries of the period are the jellium spheres with $N = 10, 60, 188, 430$, etc.

It was obtained as the next d-level is filled in turn, the previous d-state is extended. So, the most localized of d-states is upper d-level which has been fully or partially occupied. However, this state is more slowly extended than

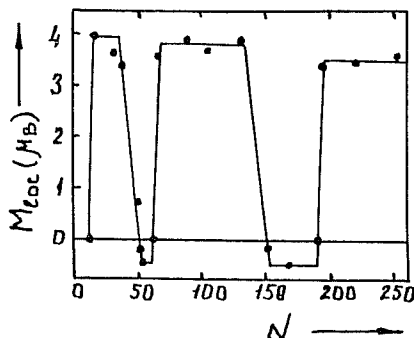
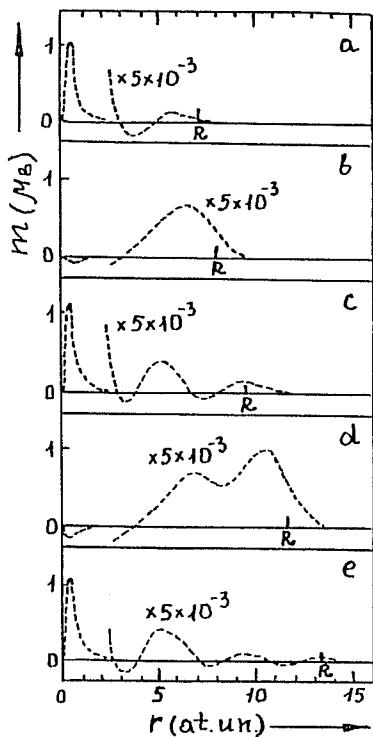


Figure 2. The magnetic moment localized near the central Fe atom in dependence on the number of electrons in the jellium sphere

Figure 1. Variation of the radial spin density distribution in the spherical-finite jellium containing the central Fe atom with the increase of the jellium sphere size: $N=32$ (a), 54 (b), 88 (c), 166 (d), 252 (e).

the d-shell of a free Fe atom, and the extent of the upper d-level increases with the rise of the jellium sphere radius.

Thus, the interaction between d-electrons of Fe atom and s-valence electrons of the Fe cluster has led to the periodical occupation of the localized d-state of the system "Fe atom in jellium" with the increase of the jellium sphere radius. Within the framework of our model this effect corresponds to the nonmonotonic change of the occupation of localized d-states with the moving away from the surface to the centre of the cluster.

The calculations of the radial spin-density distribution

$$m(r) = n_{\uparrow}^{-}(r) - n_{\downarrow}^{-}(r)$$

for the iron atom in the jellium spheres with various radii have shown that the spin-density oscillates due to the polarization of the valence electron gas by the magnetic moment of the central atom (Fig.1). The number of oscillations in the jellium sphere of the same period is equal and coincides with the number of d-levels which have been fully occupied before the start of the period. The spin density near the jellium sphere surface is positive.

The magnetic moment localized near the central atom

$$M_{loc} = 4\pi \int_0^{r_0} m(r) r^2 dr$$

oscillates with the increase of the jellium cluster size (Fig.2). These results agree with those of [3] in which the mechanism of formation of magnetic ordering near the 3d-metal surface was considered within the framework of the Anderson periodic model, and it was obtained that the magnetic moment oscillates near the surface.

The negative local magnetic moments of some jellium spheres with a central atom (see Fig.2) are caused by the negative polarization of the spin density of the closed shells near the central atom due to the exchange interaction with the open shell. The d-states of these systems are fully occupied. The open shell (or shells) is (are) near the jellium cluster surface (see Fig.1, Table 1).

We suppose that these local magnetic moment oscillations contribute to the lack of the ferromagnetic properties of small iron clusters. (On the observation of the paramagnetic character of small Fe clusters see, e.g. [1,4].)

4. REFERENCES

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