

덩어리, 단층 및 사슬 구조 철의 전자구조와 자성에 대한 LDA+U 효과

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(2009년 4월 3일 받음, 2009년 6월 4일 최종수정본 받음, 2009년 6월 4일 게재확정)

상관효과 U가 전자구조와 자성에 미치는 영향을 검토하기 위하여 대표적 자성물질인 철의 덩어리, 단층 및 사슬 구조에 대해 연구하였다. 이를 위하여 $U = 3$ eV로 택하여, 총 퍼텐셜 보강 평면파동 에너지 띠 방법을 이용하여 LDA+U 및 GGA+U 근사 하에 전자구조 계산을 수행하였다. 비교를 위하여 LDA 및 GGA를 이용한 계산도 수행하였다. 그 결과 U의 효과를 포함시켰을 때 덩어리 철의 경우 자기모멘트가 $0.3 \mu_B$ 증가하여 실험값이나 LDA 및 GGA 계산에 비해 과다하게 계산되는 것으로 나타났으나, 단층이나 사슬의 경우는 그렇게 큰 차이를 보이지 않았다. 이로부터 전자구조 계산 시 대상 계에 따라 U의 효과를 적절히 고려하여야 함을 알았다.

주제어 : 철, 결함, 전자구조, 자성

The LDA+U Effect on the Electronic Structure and Magnetism of Bulk, Monolayer, and Linear Chain of Iron

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(Received 3 April 2009, Received in final form 4 June 2009, Accepted 4 June 2009)

We examine the effect of U term ($U = 3$ eV) describing the Coulomb interactions between electrons on the results of electronic band structure calculations carried out for bcc Fe bulk, monolayer, and chain. We investigated the properties of the three Fe structures by using the all-electron total-energy full-potential linearized augmented plane wave method. The U term was included in the exchange - correlation functionals constructed on the basis of local density approximation (LDA) and general gradient approximation (GGA). We found that in the case of bcc Fe bulk structure inclusion of the U term leads to the overestimated values of magnetic moment on Fe atom. The values of magnetic moment calculated for Fe in monolayer and chain are in accordance with calculations in which the U term was not included. In general, for each system the calculated values of magnetic moment on Fe sites were larger when the U term was incorporated in the energy functional. In Fe bulk, the value of magnetic moment $2.54 \mu_B$ for LDA+U larger than $2.25 \mu_B$ for LDA.

Keywords : Fe, defect, electronic structure, magnetism

I. Introduction

An improvement of computational ab-initio methods accuracy in description of the electronic properties of solids has been an issue ever since the first theories of solids were developed. Technological progress made it possible to calculate the microscopic properties of existing materials with periodic structure, even such that contain

many types of atoms in a unit cell. Possibility to obtain reliable results for real structures let the scientists count on correct prediction of the properties of newly computer-aided designed materials. After so many years of development of first-principles methods, there is still a huge effort to implement the best possible approaches for description of specific groups of compounds. Especially challenging task is to calculate electronic structure of strongly correlated systems with the use of the methods based on density functional theory (DFT).

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The main problem in DFT-based *ab initio* calculations is the choice of exchange-correlation energy term in energy functional. At the early stage of the development of DFT-based methods, the most popular choice was such that the exchange-correlation (E^{XC}) term in the energy functional depended on electronic density in a local fashion, and so it was called the local density approximation (LDA). It is a much more difficult task to develop non-local exchange-correlation functionals. More recently, so called generalized gradient approximation (GGA) was developed to produce E^{XC} that depends not only on the electron density, but also on its gradients. This approximation works better for some systems, but still fails when strong correlation effects play important role for tailoring the electronic properties of solids. Such effects are important in systems with 3d or 4f electrons, and especially in the systems of reduced dimensionality, such as monolayers or chains. Including correlation effects in a realistic manner is difficult. A strong correlation effect between localized electrons may however be included in DFT calculations through introduction of a U term describing the effective Coulomb interactions between the electrons. With the U term added to the energy functional so-called LDA+ U and GGA+ U approaches are obtained. LDA+ U was introduced first time by Anisimov *et al.* [1] and it was proved to produce very accurate results in situations when LDA failed, like in predicting an energy gap in Mott insulators [1].

Electron correlation effects are very important in magnetic materials. A best example of such a material is iron. Pure iron has a body-centered cubic (bcc) crystal structure at room temperature and is ferromagnetic. Its magnetism is not due to the any inherent magnetic properties of the atoms, but to the structure of the metal. Therefore, surface magnetism of iron may be much different from that of the bulk.

In this paper we present the results of a first-principles calculation of the electronic and magnetic properties of bcc Fe bulk, monolayer and chain as the examples of 3-, 2-, and 1-dimensional systems with strong electron correlation. We discuss how a chosen exchange-correlation energy functional approximation necessary to solve Kohn-Sham equations influences the calculated values of certain parameters that characterize the electronic and magnetic properties of the investigated systems. We compare the properties of the three systems calculated with LDA, GGA, LDA+ U , and GGA+ U approaches.

II. Model and Computational Method

The reported calculations were carried out for bcc Fe bulk, monolayer, and linear chain. The distance between

Fe atoms in the three systems was set to 2.485 Å, regardless the reduced dimensionality. The distance is identical with the nearest neighbors distance in bcc Fe crystal. Hence, the Fe monolayer represented a single layer of Fe (001) surface.

The Kohn-Sham equation was solved self-consistently in terms of the full-potential linearized augmented plane wave (FLAPW) method [2, 3] as embodied in the QMD-FLAPW code with LDA [4], GGA [5], as well as with the LDA+ U and GGA+ U approaches, in which an additional Hubbard- U term was added [1, 6] for the treatment of strong on-site 3d electron - electron interactions on Fe, which we used as $U = 3$ eV. Lattice harmonics with $l \leq 8$ were employed to expand the charge density, potential, and wave functions inside the muffin-tin (MT) radii of 2.348 atomic unit (a.u.) for the Fe atom. A plane wave cut-off of 16 Ry was employed, and so more than 100 basis functions per atom were used to expand the wave functions. Integration was performed by summation over 84, 36, and 11 k-points for the bulk, the monolayer, and the chain inside the irreducible Brillouin zone. All core electrons were treated fully relativistically, while valence states were treated scalar relativistically. Self-consistency was assumed when the difference between input and output charge (spin) density was less than 1.0×10^{-5} electrons/(a.u.)³.

III. Result and Discussion

There have been continuous experimental and theoretical studies to examine the magnetic properties of iron surfaces and thin films [1]. Many studies have been also devoted to the investigations of the properties of systems with reduced dimensionality, such as monolayers, nanowires and chains. Especially accurate studies of iron low-dimensional structures (thin films, monolayers, and chains) have been carried out with the use of FLAPW [1, 6-12]. The early theoretical works devoted to the magnetism of iron surfaces, monolayers and chains reported the use of local (spin) density approximation (L(S)DA) for the energy functional. With that approach, Weinert and Freeman [10] predicted a large magnetic moment (MM) of $3.3 \mu_B$ for an Fe chain, in which the atoms were separated by 2.488 Å, that is by the distance equal to the nearest neighbors distance in bcc bulk. As it comes to a Fe monolayer cut from Fe (001) surface, Fu *et al.* [11] calculated the value of MM on Fe atom in the monolayer equal to $3.20 \mu_B$. Hence, it was found that the values obtained for both the chain and the monolayer are much larger than that on Fe atom in the bcc bulk. Later, Ying *et al.* [12] discussed the properties of Fe chains in different environment with the

use of the same FLAPW method within GGA. They calculated MM on Fe atom in an isolated chain to be $2.99 \mu_B$. Even though the distance in the chain was by 0.068 \AA larger than in the chain investigated by Weinert and Freeman, such a big discrepancy between the obtained values of MM on Fe atom must have resulted from another factor, which in that case was a different approximation to the energy functional. This comparison shows that it is important to choose an appropriate functional that will predict the accurate ground-state magnetic properties of low-dimensional iron systems.

The values of MM on Fe atom in the investigated bulk, the monolayer and the linear chain calculated with different approaches (LDA, LDA+U, GGA, and GGA+U) are collected in Table I together with the calculated values of work function for the monolayer and the chain. The l -decomposed majority (\uparrow) and minority (\downarrow) spin charges (in electrons) inside Fe MT sphere are also given.

As it is seen from the Table, the value of MM on Fe atom increases with the reduced dimensionality of the Fe structure, and the overall tendency does not depend on the chosen approach. However, there are considerable differences between the results obtained with and without the U term included in the energy functional. For the Fe bulk structure, using the LDA (GGA), we obtained the value of MM equal to 2.25 (2.29) μ_B , which is close to the experimental value. Insertion of the U term in the energy functional caused that the calculated value of MM are overestimated: $2.54 \mu_B$ for LDA+U and $2.60 \mu_B$ for GGA+U, respectively. The tendency for LDA+U and GGA+U to give larger values of MM on Fe atom is also

observed in the case of the monolayer and the chain. However, in the low-dimensional structures, the differences between the values of MM obtained with LDA and LDA+U and GGA and GGA+U approaches are much smaller than those calculated for the bulk. Using LDA, we calculated the MM on Fe atom in the monolayer to be equal $2.97 \mu_B$, which is much smaller than the value reported by Fu *et al.* ($3.20 \mu_B$) obtained with the same method [11]. However, in their model monolayer the distance between atoms was exactly equal to the bcc Fe lattice constant, while in our calculations the atoms are separated only by the distance between the nearest neighbors in bcc Fe.

It is easier to compare our results obtained for the chain with the available data in the literature. With LDA we obtained the value of MM on Fe atom in the chain equal to $3.23 \mu_B$, which is only slightly smaller than that reported by Weinert and Freeman [4]. The result obtained with GGA ($3.23 \mu_B$) differs by 8 % from that presented by Ying *et al.* [12]. However, the distance between Fe atoms in the chain investigated by our group was smaller, which may be the cause for the difference. The values of the MM calculated with LDA+U or GGA+U approach in the case of the chain are merely larger than those obtained with just LDA or GGA. Hence, with the reduced dimensionality of Fe system the differences between the values of MMs obtained with or without the U term included in the energy functional become smaller and less meaningful.

The MM on atoms is the measure of a difference between the numbers of electrons with spin up and spin down localized within the MTs of the atoms. In Table I,

Table I. The magnetic moment, and l -decomposed majority (\uparrow) and minority (\downarrow) spin charges (in electrons) inside the MT spheres for bulk, monolayer and linear chain of Fe, and work functions (ϕ) for monolayer and linear chain.

Bulk						
	s (\uparrow/\downarrow)	p (\uparrow/\downarrow)	d (\uparrow/\downarrow)	Total (\uparrow/\downarrow)	MM (μ_B)	ϕ (eV)
LDA	0.21/0.22	0.20/0.24	4.22/1.94	4.65/2.40	2.25	-
LDA+U	0.20/0.22	0.18/0.23	4.39/1.80	4.81/2.26	2.54	-
GGA	0.21/0.22	0.19/0.25	4.24/1.90	4.66/2.38	2.29	-
GGA+U	0.20/0.22	0.18/0.24	4.43/1.75	4.83/2.27	2.60	-
Monolayer						
LDA	0.22/0.19	0.10/0.09	4.51/1.59	4.85/1.88	2.97	4.84
LDA+U	0.23/0.20	0.11/0.10	4.56/1.50	4.91/1.81	3.10	4.74
GGA	0.22/0.19	0.10/0.10	4.53/1.56	4.86/1.86	3.00	4.03
GGA+U	0.23/0.20	0.10/0.10	4.58/1.49	4.91/1.80	3.10	4.29
Chain						
LDA	0.26/0.19	0.05/0.04	4.60/1.46	4.91/1.69	3.23	4.47
LDA+U	0.27/0.21	0.06/0.05	4.62/1.37	4.94/1.63	3.31	4.14
GGA	0.26/0.19	0.05/0.04	4.60/1.46	4.92/1.69	3.23	3.76
GGA+U	0.26/0.20	0.06/0.05	4.60/1.42	4.92/1.67	3.25	3.72

the l -decomposed charges with spin up and spin down are shown for the each investigated structure. As it is known the DFT (either LDA or GGA)+U approach enforces both a pure Coulomb interaction between electrons in an open shell. Therefore, there must be some changes in the charges within Fe MT calculated with and without the U term in the energy functional. Indeed, looking at the numbers of d electrons calculated for the bcc Fe bulk structure one can see that incorporation of the U term causes that the number of charges with spin up on Fe site becomes larger, and that of spin down is reduced comparing with the results obtained with LDA and GGA. The number of charges in s and p shells does not change considerably; therefore it may be concluded that in calculations done with the use of LDA or GGA a portion of electrons is spread into the interstitial region, while incorporation of a strong electron-electron correlation causes a larger separation of electrons with different spin and a stronger bounding of the electrons with the Fe atom. Again, when the dimensionality of Fe structure is reduced, the differences between the calculated values of l -decomposed charges with various approaches are getting smaller. There is a remarkable difference between the numbers of p electrons inside the Fe MT in the three structures. In both the monolayer and the chain the number of p electrons is much smaller than the number of the electrons in the bcc Fe bulk. This is because of the sudden termination of periodicity in one or two directions. In the case of the monolayer, p electrons spill out into the vacuum region and in the case of the chain the electrons spread out additionally into interstitial region.

An informative parameter for the discussion of the electronic properties of systems with a reduced dimensionality is the value of a work function. Generally, GGA calculations give much smaller values for the work function than LDA ones. The results collected in Table I indicate that the results of our calculations are in agreement with that rule. As far as the comparison between the results obtained with and without U term is concerned, we noticed that including the electron-electron correlation causes that the value of work function obtained with a certain approach is smaller than that calculated without electron correlation considered. This is true for all the cases but one: the value of work function calculated for the monolayer with GGA+U approach is surprisingly larger than that calculated with GGA.

IV. Conclusions

We tested the application of different exchange-correlation energy functional to the calculations of the electronic and magnetic properties of iron in three different systems that had different dimensionality, i.e. bulk, monolayer, and linear chain. We used LDA, LDA+U, GGA, and GGA+U approaches. We found that the calculated values of the parameters characterizing the electronic and magnetic properties of the investigated systems are different depending on which approximation (LDA or GGA) is used. We also noticed that introduction of the electron-electron correlation factor causes that the results vary even for the same energy functional approximation. However, the differences between DFT (LDA or GGA) and DFT+U results become smaller when the system dimensionality is reduced.

The results of our study indicate that the systems containing ferromagnetic transition metal, such as iron, are very delicate and one should be very careful to choose the best possible approach to find the most accurate results of the electronic structure calculations.

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