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Distinct magnetic states of metastable fcc structured Fe and Fe–Cu alloys studied by ab initio calculations

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Abstract

Based on the projector augmented wave method within the generalized gradient approximation, ab initio calculations predict five distinct magnetic states of Fe in fcc structure depending sensitively on their atomic volumes, i.e., with increasing the atomic volume, there appears firstly a complicated coexistence of a non-magnetic, two antiferromagnetic, and a low spin ferromagnetic states, and then a high spin ferromagnetic state. Moreover, the present calculations also predict that the high spin ferromagnetic state of Fe atoms could be stabilized in some non-equilibrium Fe–Cu alloys over a relatively broad composition range, suggesting a possible approach to synthesize new Fe-containing alloys of high performance in magnetization. An intensive discussion is accompanied to compare the predictions with those from experiments as well as from those calculated results reported previously. It turns out that the present calculations could give reasonable interpretation to the richness and/or the complexity of the magnetic behaviors of fcc Fe and the Fe–Cu alloys.

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1. Introduction

Among the ferromagnetic transition metals (Fe, Co, Ni), Fe has the highest moment, which makes the Fe containing materials useful in hi-tech applications requiring high magnetization. Meanwhile, due to its not fully filled d band, the magnetic moment of Fe in an alloy is changeable and varies in a broad range from 0 to 3 μ_B, depending on the structure and composition of the materials. The magnetic properties of Fe have thus attracted great attention, especially the magnetic property of the metastable fcc Fe and fcc structured Fe-containing alloys. In this respect, however, the results obtained so far from various investigations show some complexity and sometimes are even controversy. For instance, it has been reported that fcc Fe could be anti-ferromagnetic (AFM) and/or ferromagnetic (FM) and that the magnetic moments per Fe atom were different while Fe atoms locating at different atomic sites in thin films or in a reconstructed surface, etc. [1–3]. Besides, neutron scattering, Mössbauer and other magnetic measurements have also revealed the richness of the magnetic orderings of Fe [4]. The richness in magnetic states and close competition between different magnetic states of fcc Fe have been confirmed by various first principles total energy calculations [5–9]. In general, the previous calculations predicted that the non-magnetic (NM) or paramagnetic, FM, and AFM states were quite close in energy and that the relative stability of a specific state depends sensitively on the atomic volume of the Fe atom in the state. For instance, some of the previous calculations predicted an AFM ground state at a small atomic volume, while a high-spin ferromagnetic (HSFM) ground state at a large atomic volume. Recently, a new first-principles calculation approach named the projector augmented wave method (PAW) was proposed by Blöchl [10] and is expected to be able to handle even the most difficult issues with improved precision, especially in treating with the transition metals [11]. We therefore employ the PAW method, in the present study, to carry out a series of

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calculations for further clarifying the structural stability and magnetic orderings of metastable fcc Fe.

In spite of some difference in the calculation methods, almost all the calculations suggested that the fcc structured Fe was the most important/interesting issue, because it could possess a highest magnetic moment per atom among all the equilibrium/non-equilibrium states of the 3d ferromagnetic elements, which, to authors' view, could be an important theoretical guidance for designing and fabricating new materials of high magnetic performance. In this sense, there are two important aspects for further studies. First is to soundly confirm the existence of the HSFM state by experiments, which, from a philosophical point of view, is necessary for a complete recognition of the state. Second is to find out if some non-magnetic fcc structured elements, e.g. the noble metals of Cu, Ag and Au, could form some alloys with Fe to help in stabilizing the Fe in the HSFM state, as fabrication of pure and bulk fcc Fe is almost impossible. Consequently, investigating the magnetic properties of Fe-noble metal alloys is of vital importance. In this regard, however, the previous studies have only been concentrated on the structural and magnetic properties of Fe grown on the Cu substrates or in the Cu matrices and/or non-equilibrium Fe–Cu solid solutions, yet little attention has ever been paid to the possible non-equilibrium Fe–Cu intermetallic compounds, in which Cu alloying might play an indispensable role in stabilizing the HSFM state of fcc Fe. Accordingly, calculation of the structural stability and the associated magnetic property of the possible non-equilibrium Fe–Cu intermetallic compounds is another important objective of the present study with an aim to provide some guidance for developing new materials of high performance.

2. Calculation method

The calculations were carried out by using the Vienna ab initio simulation package VASP [12–14] based on the projector augmented wave pseudopotential [10,11]. In the present study, the $3d^74s^1$ state is treated as the valence for the PAW pseudopotential of Fe. The exchange and correlation effects were described by the functionals proposed by Perdew and Zunger [15], with generalized gradient corrections [16]. Brillouin-zone integrations were performed according to the Monkhorst–Pack scheme [17]. For calculations of pure Fe, a plane-wave energy cutoff of 334.9 eV was used, and while treating the Fe–Cu alloys, a cutoff of 341.6 eV was employed. Besides, for all spin polarized calculations, the Vosko–Wilk–Nusair interpolations were used for the correlation part of the exchange correlation functional [18].

3. Magnetic orderings of fcc Fe

The energy–volume correlation of bcc Fe is first calculated and then fitted to the Murnaghan Equation of State [19] to obtain its cohesive property as well as to certify the validity of the present calculation method. We find a FM ground state for the bcc Fe, and its lattice constant, magnetic moment, and bulk modulus are calculated to be 2.83 Å, 2.21 μ_B and 1.76 Mbar, respectively, which are in inspiringly good agreement with the experimental data of 2.87 Å [20], 2.22 μ_B [21], and 1.72 Mbar [21], respectively, as well as with those calculated by Kresse et al. who treated $3d^{6.5}4s^{1.5}$ as valence for the PAW pseudopotential of Fe [11].

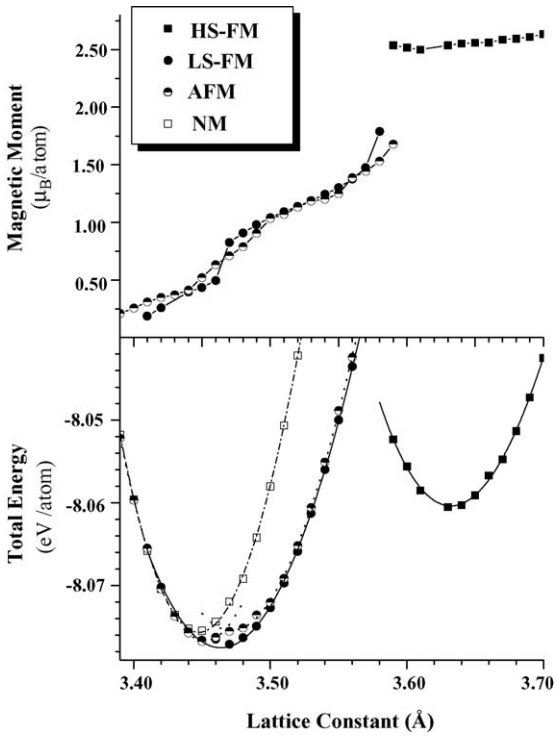

Fig. 1. Correlations of total energies (lower panel) and magnetic moments (upper panel) against the lattice constant of fcc iron obtained by ab initio calculations within the GGA.

The above agreements certify the validity of the present calculation method, based on which further study is pursued to investigate the magnetic orderings of fcc Fe. Fig. 1 shows the calculated correlations of the total energy and the corresponding magnetic moment versus the lattice constant for fcc Fe with different magnetic orderings. The fitted cohesive properties and the magnetic moments are listed in Table 1, together with some values cited from the available experimental results and/or from the previous calculations. As can be seen, firstly, all the fcc phases of Fe have a positive heat of formation with respect to the bcc FM ground state of Fe, which is consistent with the well-known fact that the FM bcc phase is the equilibrium state of Fe at low temperatures. Secondly, the predicted cohesive properties of different fcc states are quite compatible with the experimental results and/or the previous calculations. Thirdly, the fcc Fe shows rather complicated magnetic orderings, depending sensitively on its spacing distance.