

STRUCTURE AND MAGNETISM OF IRON AND IRON OVERLAYERS FROM THE FIRST PRINCIPLES

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ABSTRACT

A detailed theoretical study of magnetic behavior of iron along the bcc-fcc (Bain's) transformation paths at various atomic volumes is presented. The total energies are calculated by spin-polarized full-potential LAPW method and are displayed in contour plots as functions of tetragonal distortion c/a and volume; borderlines between various magnetic phases are shown. Stability of tetragonal magnetic phases of γ -Fe is discussed. The calculated phase boundaries are used to predict the lattice parameters and magnetic states of iron overlayers on various (001) substrates.

KEYWORDS

Electronic structure, magnetism of iron, iron overlayers, metallic thin films

INTRODUCTION

Iron thin films and overlayers on various metallic substrates have attracted a lot of interest in recent years [1–14]. They exhibit a rich variety of magnetic phases. For example, on the (001) surface of Ag, Pd and Cu_3Au , they are ferromagnetic (FM). On $\text{Cu}_{84}\text{Al}_{16}$ and on Cu, both ferromagnetic and antiferromagnetic (AFM) ordering was observed. In addition to that, considerable differences in magnetic properties of pulsed-laser-deposited and thermally deposited iron films on Cu(001) were reported [10]. All this is connected with the fact that the density of the iron films on Cu and $\text{Cu}_{84}\text{Al}_{16}$ is very close to the range for which a longitudinal spin-density instability was predicted in bulk γ -Fe [15]. At these densities, ferromagnetic high-spin and low-spin states and antiferromagnetic states differ only very little in energy and, therefore, the magnetic ground state of iron films on those substrates will depend critically on volume and symmetry. The experimental results for (001) iron thin films and overlayers on various substrates are collected in Table 1, where the substrates are given in decreasing order of lattice constants.

Pseudomorphic iron overlayers adopt the lattice dimensions of the substrate in the (001) plane and relax the interlayer distance. This typically results in a strained tetragonal structure of the film. There is a stress in the (001) plane keeping the structure of the film

and of the substrate coherent, and the stress perpendicular to this plane vanishes due to relaxation. A tetragonal phase arises, which may be stable or metastable [16]. Iron films and overlayers on (001) substrates have, therefore, a tetragonal structure (Fig. 1).

Table 1. Type of magnetic ordering of iron overlayers on (001) substrates (experimental results). FM denotes ferromagnetic ordering, AFM antiferromagnetic ordering, a_{sub} is the lattice constant of the substrate.

substrate	a_{sub} (Å)	magnetic ordering (Fe)	reference
Ag	4.086	FM	[1, 2]
Pd	3.891	FM	[3]
Rh	3.804	not determined yet	[4]
Cu ₃ Au	3.745	FM	[5, 6]
Cu ₈₄ Al ₁₆	3.649	FM/AFM	[7]
Cu	3.615	FM	[8, 9, 10]
Cu	3.615	AFM	[11, 12, 10]
Ni	3.524	not determined yet	[13, 14]

To advance our fundamental understanding of energetics of tetragonal iron, we performed ab initio calculations of electronic structure (ES) and total energy along tetragonal (Bain's) deformation paths at various volumes [17]. It turns out that the results of these calculations may be used to understand and predict the structure and magnetic ordering of iron overlayers on (001) substrates. The purpose of the present paper is to discuss this application in more detail.

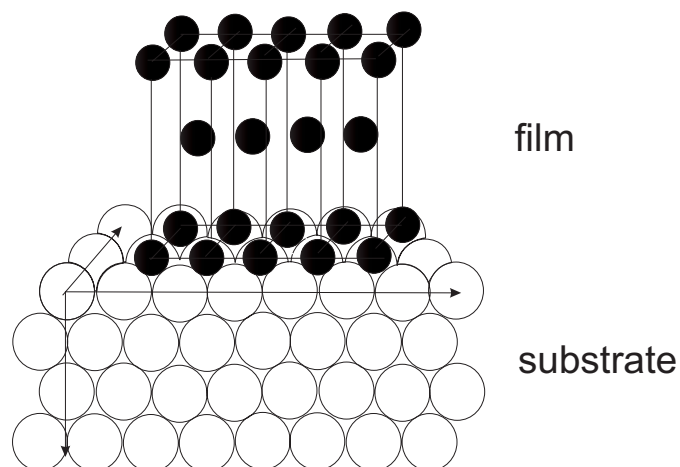


Figure 1: Epitaxial growth of overlayers on a (001) substrate.

METHODOLOGY

Craievich et al. [18] have shown that some energy extrema on constant-volume transformation paths are dictated by the symmetry. Namely, most of the structures encountered along the transformation paths between some higher-symmetry structures, say between bcc and fcc at the Bain's path, have a symmetry that is lower than cubic. At those points of the transformation path where the symmetry of the structure is higher the derivative

of the total energy with respect to the parameter describing the path must be zero. These are the so-called symmetry-dictated extrema. However, other extrema may occur that are not dictated by symmetry and reflect properties of the specific material. Configurations corresponding to energy minima at the transformation paths represent stable or metastable structures and may mimic atomic arrangements that could be encountered when investigating thin films [16] and extended defects such as interfaces and dislocations [19, 20].

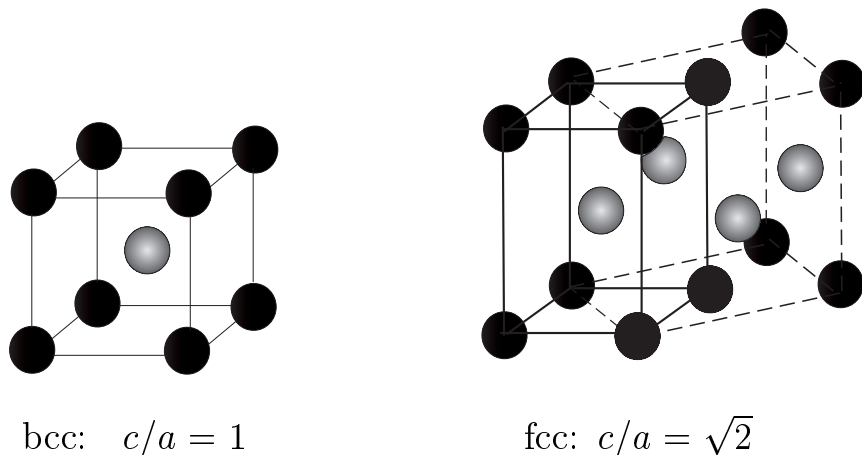


Figure 2: bcc and fcc structures along the tetragonal deformation path.

We start with the bcc structure and consider it as a tetragonal one with the c/a ratio equal to 1. Subsequently, we perform a tetragonal deformation (uniaxial deformation along the [001] axis), i.e. we change the c/a ratio and the structure becomes tetragonal indeed. However, at $c/a = \sqrt{2}$, we arrive to the fcc structure, which has again cubic symmetry (Fig. 2). The points $c/a = 1$ and $c/a = \sqrt{2}$ correspond to the only high-symmetry structures along the tetragonal deformation path and, therefore, symmetry-dictated extrema of the total energy may be expected here [18, 19]. Let us note that many papers define the c/a such that the fcc structure is considered as a tetragonal one with $(c/a)^* = 1$; then $(c/a)^* = (c/a)/\sqrt{2}$ and the bcc structure corresponds to $(c/a)^* = \sqrt{2}/2$.

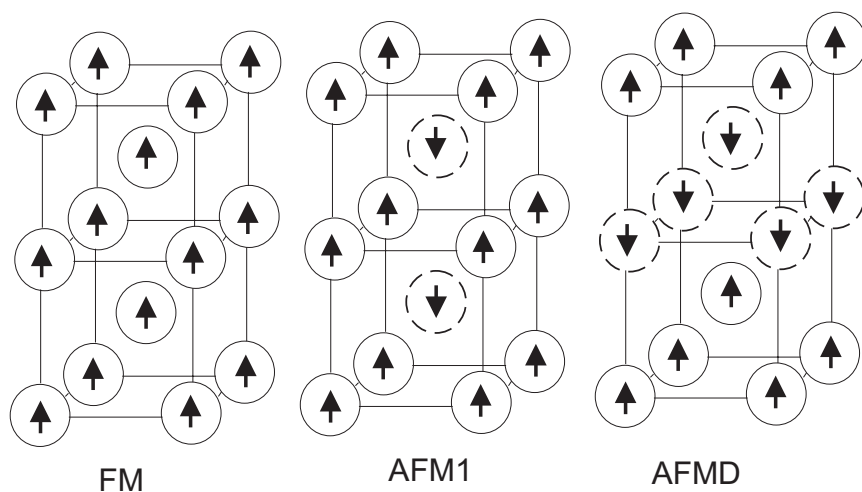


Figure 3: Ferromagnetic (FM) and antiferromagnetic single-layer (AFM1) and double-layer (AFMD) states.

We calculate total energy of iron along the tetragonal deformation paths keeping the atomic volume constant; the region of atomic volumes studied extends from $V/V_{exp} = 0.84$ till $V/V_{exp} = 1.05$. We include nonmagnetic (NM), ferromagnetic (FM) and two anti-ferromagnetic states (Fig. 3), namely the single-layer antiferromagnetic one (AFM1), in which (001) planes have alternating magnetic moments ($\uparrow\downarrow\uparrow\downarrow \dots$), and double-layer one (AFMD), where the pairs of (001) planes have alternating magnetic moments ($\uparrow\uparrow\downarrow\downarrow \dots$).

For the electronic structure calculations, we utilized the full-potential linearized augmented plane waves (FLAPW) WIEN97 code described in detail in [21]. The FLAPW method is one of the most accurate ab initio (first-principles) methods for calculating electronic structure of solids. Here the electron wave functions are expressed as a linear combination of convenient basis functions and the total energy of the system is minimized by means of the variational principle. This approach leads to the system of Kohn-Sham equations that must be solved selfconsistently, and this is the primary computational task. The total energy itself consists of a few parts; a special attention is paid to the exchange-correlation part which emerges from the density functional theory (DFT) of Hohenberg, Kohn and Sham.

The FLAPW method employs a combined system of basis functions. Inside of non-overlapping so-called muffin-tin spheres constructed around each nucleus, radial Schrödinger equation is solved and a linear combination of its solutions (radial functions) multiplied by spherical harmonics is used to express the electronic wave functions in this region. In the remaining space (interstitial region) the electronic wave functions are described by a linear combination of plane waves. The condition that basis functions inside the muffin-tins must match the corresponding basis functions (plane waves) in the interstitial region on the sphere boundary in value and slope determines certain coefficients in the expression for the basis functions and such basis functions are called "augmented plane waves".

For the above mentioned exchange-correlation part of the total energy, the local density approximation (LDA) or its spin-polarized version (LSDA) is relevant for most problems. Unfortunately, it fails in case of some important materials, e.g. it predicts an incorrect ground state of iron. One way how to go beyond the LDA is so-called generalized gradient approximation (GGA); it includes gradients of the electronic density and fixes some problems as e.g. the ground state of iron mentioned above. In the present paper, all electronic structure calculations were performed self-consistently within the GGA [22]. The muffin-tin radius of iron atoms of 1.90 au was kept constant for all calculations, the product of the number of $\mathbf{k}$ -points and number of non-equivalent atoms in the basis was equal to 6000, and the product of the muffin-tin radius and the maximum reciprocal space vector, $R_{MT}k_{max}$, was equal to 10. The maximum ℓ value for the waves inside the atomic spheres, ℓ_{max} , and the largest reciprocal vector $\mathbf{G}$ in the charge Fourier expansion, G_{max} , was set to 12 and 15, respectively.

RESULTS AND DISCUSSION

Fig. 4 displays the variation of total energies of iron along the tetragonal deformation path at the experimental lattice volume of the FM bcc iron of $11.72 \text{ \AA}^3$ and at the atomic volume of $10.21 \text{ \AA}^3$.

The NM and FM states exhibit energy extrema at $c/a = 1$ and $c/a = \sqrt{2}$ corresponding to higher-symmetry structures (bcc and fcc). However, the AFM1 iron keeps its cubic

symmetry only for $c/a = 1$, i.e. for the bcc structure. At $c/a = \sqrt{2}$, the atoms occupy the fcc lattice positions, but as the atoms with spins *up* and *down* are not equivalent, the resulting symmetry is tetragonal, exactly the same as the symmetry of the structures in the neighborhood of the $c/a = \sqrt{2}$, and no higher-symmetry structure occurs here. Therefore, no symmetry-dictated extremum of total energy at $c/a = \sqrt{2}$ is to be expected. And, indeed, the total energy curves of AFM1 states exhibit, in general, a non-zero derivative at $c/a = \sqrt{2}$ (Fig. 4); this was also found by Qiu *et al.* [23]. The minima of the AFM1 curves are not dictated by symmetry. As to the AFMD iron, it is never cubic and no symmetry-dictated extrema occur along the tetragonal deformation path.

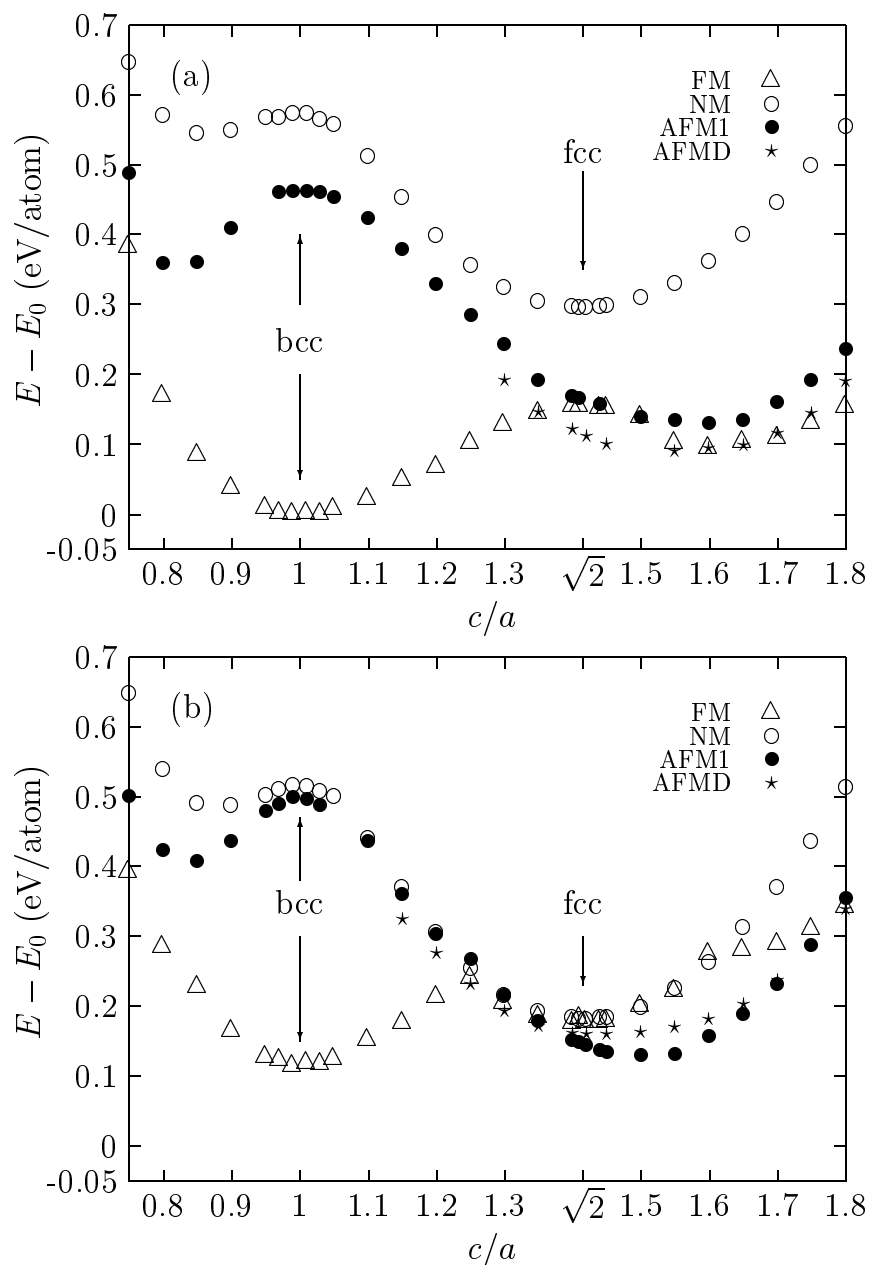


Figure 4: Variations of total energies of iron along the constant-volume bcc–fcc transformation path at the experimental atomic volume $V_{exp}=11.72 \text{ \AA}^3$ (a) and at the atomic volume $V=10.21 \text{ \AA}^3$ (b) relative to the equilibrium energy E_0 of FM bcc iron.

It may be seen from Fig. 4a that the FM bcc iron has the lowest energy at the experimental atomic volume. In the region from $c/a \approx 1.4$ till $c/a \approx 1.7$, the AFMD ordering is

most favorable. This situation is somewhat changed at sufficiently lower atomic volumes. At $V = 10.21 \text{ \AA}^3$, the energy of the FM bcc state is still the lowest one. However, for $1.4 \lesssim c/a \lesssim 1.8$, the AFM1 states are most favorable.

The total energy of iron as a function of volume and tetragonal deformation may be seen in Fig. 5. Here we show only those states the energies of which are the lowest for a given configuration. We can clearly see the "horseshoes" dividing the plane into the AFM1, AFMD and FM regions. The global minimum of energy is in the FM region at $c/a = 1$, $V/V_{exp} = 0.985$, which corresponds to the bcc structure. The calculated equilibrium volume is about 1.5 % lower than the experimental value, which may be considered as a very good agreement.

The total energy profile of bulk iron presented in Fig. 5 enables us to predict easily the lattice parameters and magnetic states of iron overlayers at (001) substrates. Let us suppose that the pseudomorphic iron overlayers adopt the lattice dimensions of the substrate in the (001) plane and relax the interlayer distance (characterized by c/a). If the lattice constant of a fcc substrate is equal to a_{sub} , then, in the coordinates $x = c/a$, $y = V/V_{exp}$ and $z = E - E_0$, the surfaces corresponding to a fixed a_{sub} in the (001) planes are the planes $y = kx$, where $k = (\sqrt{2}/8)(a_{sub}^3/V_{exp})$. The configuration and magnetic state of iron overlayers on a (001) substrate should correspond to the energy minimum constrained to this plane provided that the effect of the substrate/overlayer interface is not very strong. In Fig. 6, these planes for different values of a_{sub} are displayed by straight lines together with available experimental results and our theoretical predictions.

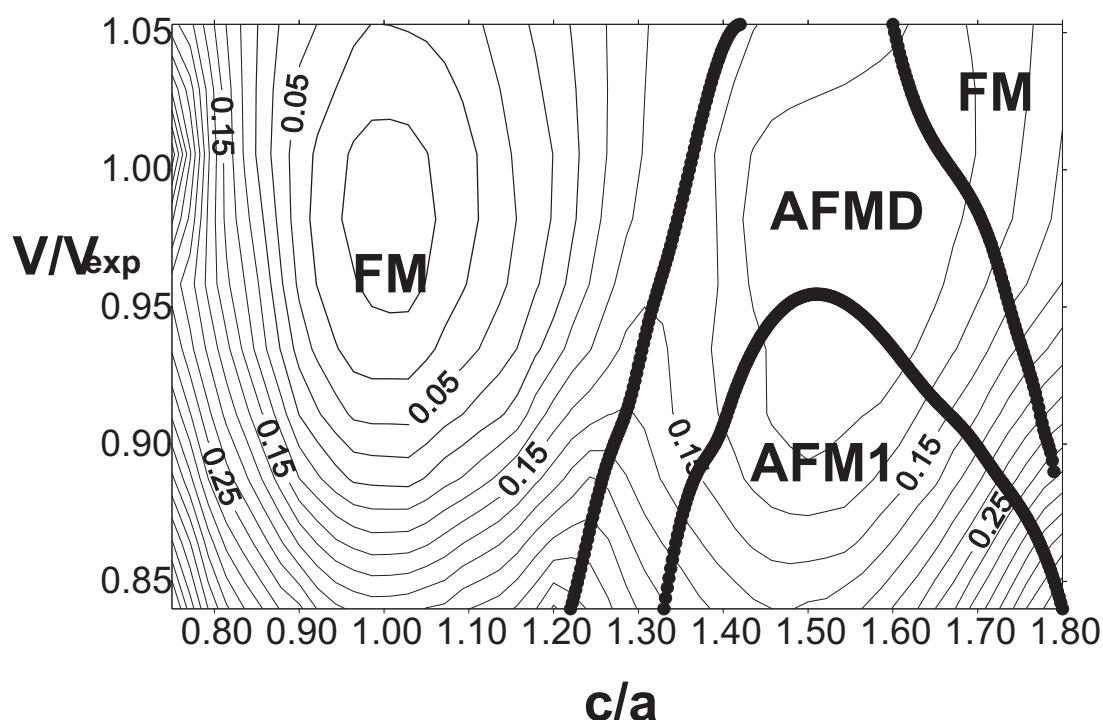


Figure 5: Total energy of iron as a function of c/a and volume relative to the FM bcc equilibrium state energy calculated within the GGA. Only states with minimum energy are shown. The contour interval is 20 meV/atom. Thick lines show the FM/AFMD and AFMD/AFM1 phase boundaries.

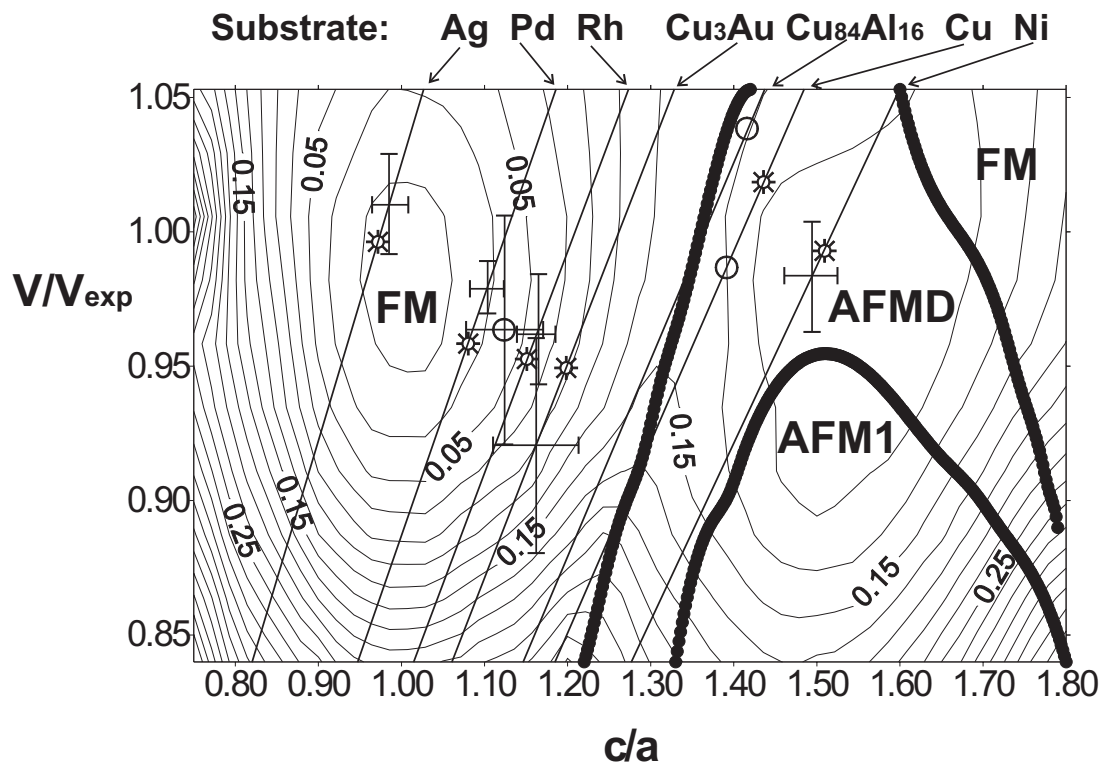


Figure 6: The same as in Fig. 5, but with the added straight lines corresponding to constant lateral lattice parameters of various (001) substrates, as described in the text. The crosses composed from the vertical and horizontal error bars centered at those straight lines represent the structures of Fe films on the corresponding substrates found experimentally. One of these crosses is out of the line; it stands for the experimental structure of Fe/Cu₃Au(001) films found in [6] and its center is denoted by an open circle. The other two open circles show the experimental structures where no error bars were given. Smaller open circles combined with asterisks represent theoretical results found in [17].

The experimental point for Fe films on Ag(001) is taken from [1]. It corresponds to a slightly distorted bcc structure and lies in the FM region, in agreement with experimental findings [2]. Our theoretical point is within the experimental limits. A similar situation takes place for Fe films on Pd(001) [3] and Rh(001) [4]. The films exhibit body centered tetragonal structure and the theoretical results are not very far from the experimental ones (for Rh, we are again within experimental limits). The points for Fe films on Pd and Rh substrates still lie in the FM region. The FM ordering of films on Pd was also confirmed experimentally [3], as to the Rh substrate, the magnetic structure of the films was not investigated yet [4].

As for Cu₃Au(001) substrate, there are two experimental findings for thin films. One of them [5] lies at the straight line for the Cu₃Au substrate in Fig. 6, and our theoretical point is within the experimental limits. The other one [6] is somewhat shifted from the Cu₃Au line. The structure of the films corresponds again to a tetragonally strained FM bcc phase, in agreement with experiment [6].

Fe films on Cu₈₄Al₁₆(001) are reported to be fcc with the volume of 12.15 Å³ [7]. The corresponding point lies very close to the phase boundary between the FM and AFMD

ordering in the fcc region. This is also in accordance with experimental findings – up to 4 ML, high-spin FM state is reported, for higher thicknesses a low-spin and/or AFM phase was found [7]. Here we do not have enough calculated results to find out the theoretical point, but it will not be probably too much higher than $(c/a, V/V_{exp}) = (1.44, 1.05)$.

Another system close to the FM/AFMD phase boundary are the Fe films on Cu(001). This fact confirms a conclusion of Ref. [24] that FM and AFMD phases are energetically almost degenerate along the line corresponding to the lattice constant of Cu and somewhat favored over the AFM1 phase, and is closely connected with a variety of magnetic states found in the Fe films on Cu(001). Our theoretical point lies in the AFMD region and is not very far from the experimental result [25] (see Fig. 6).

Finally, the straight line for Fe films on Ni(001) is, for lower volumes, close to the AFMD/AFM1 phase boundary. However, the experimental point [13] is distinctly in the AFMD region, and our theoretical prediction lies again within the experimental limits. In reality, however, magnetic polarization due to FM Ni substrate may induce FM order in the film [14].

CONCLUSIONS

In conclusion, we have calculated the total energies of iron as a function of volume and tetragonal distortion and found the minimum energies and borderlines between various magnetic phases. The calculated contour plot has been used for understanding and prediction of lattice parameters and magnetic states of Fe films on various metallic substrates; our theoretical results are in a very good agreement with available experimental data. Further, we have confirmed that the antiferromagnetic fcc γ -Fe is not stable with respect to tetragonal distortion.

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