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Effects of hydrogen absorption on physical properties of $\gamma'-Fe_4N$

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ABSTRACT

Ab initio calculations (VASP) are performed on hydrogen containing Fe_4N : Fe_4NH_n, $n = 0, 1, 2, 3$. Effects of hydrogen on structural and magnetic properties are pointed out. For $n = 3$ the calculated magnetization (177 emu/g) is close to the experimental value obtained from oxalate precursors in fluidized bed reactors. From this result, we show some drawbacks of this solid state method of synthesis for Fe_4N magnetic particles.

1. Introduction

In the nineties a lot of research was devoted to high density magnetic recording. These works, experimental as well as theoretical, have led us to consider new particulate media with specific properties. High saturation (σ_s) and remanent (σ_r) magnetizations, large coercive fields on one hand and specific morphologies on other hand were required. Among the proposed materials, iron nitride $\gamma'-Fe_4N$ was intensively studied due to its high value of σ_s—208 emu/g [1]—(very close to that of pure iron 218 emu/g), its enhanced resistance to air reactivity and the possibility of achieving a good control of the size and morphology of the magnetic particles.

More recently, highly efficient spin-electronics devices have been developed for applications to magnetic memories and magnetic sensors. A typical device presents ferromagnetic tunnel junctions consisting of a ferromagnetic electrode (FME)/insulator/(FME), which exhibits a large magnetoresistance effect [2]. It was found that ferromagnets consisting of magnetic metals and *lights elements*, such as CoFeB in CoFeB/MgO/CoFeB junctions might be very efficient as electrodes [3]. From a metallurgical viewpoint, this light element is a glass-former but it also plays a crucial role on spin-polarized transport. As such ferromagnetic systems are put into consideration, iron nitrides also present a renewed interest. For example, junctions like Fe_4N/MgO/CoFeB [4] or Fe_3N/AlN/Fe_4N were studied [5].

As concerns fine particles for magnetic recording, the best route to obtain the desired specifications was to start from a submicrometer-sized acicular precursor like iron oxalate or goethite and to transform it by a pseudo-isomorphic process. The decomposition of the precursor particles was best achieved through reducing and nitriding conditions using a fluidized bed reactor [6] which ensures good contact between the reacting gas and solid particles. The reaction atmosphere was a gas mixture of NH_3 and H_2 with an NH_3/H_2 ratio close to unity. A typical preparation needed a thermal treatment temperature around 400 °C lasting 4 h.

Most of the experimental studies performed at this time concerned the improvement of coercive fields by appropriate substitutions of different metals for iron (Sn, Ru, Os, Ni, Mn, etc. [7,9]) or surface coating of the particles [10]. The control of saturation magnetization was not considered as this value was high enough. Nevertheless the optimum expected value of 208 emu/g was never obtained for pure powders. Whatever the experimental conditions, $\sigma_s$was lower with values around 150–180 emu/g. More recently similar experiments have shown a decrease of the magnetization from 220 to 188 emu/g according to the ammonia flow [8]. Among other possible reasons, these results suggest that a certain amount of hydrogen should be present in the final iron nitride powders. Such hydrogen insertion may be responsible for the modifications of nitride properties, especially the poor value of σ_s. In order to check this important

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point and to estimate the amount of hydrogen adsorbed in the compound we performed band structure calculations on $\gamma'-Fe_4NH_n$, $n = 1, 2, 3$.

2. Computational details and approximations

The projector augmented-wave (PAW) method [11] provides the DFT framework of the calculations. The first-principles numerical experiments have been performed using the Vienna *ab initio* simulation package (VASP) [12,13] within the generalized gradient approximation (GGA). The Vosko–Will–Nussair interpolation formula [14] is used for the correlation part of the exchange correlation functional in the context of PW91 approximation. The interaction between ions and electrons is described by the PAW method implemented by Kresse and Joubert [15]. The plane wave energy cut-off is 555 eV. For each system the k-point mesh is refined (256 special k-points) until the total energy converges within 1 meV/atom. A Gaussian smearing of 0.1 eV has been applied for Brillouin zone integrations.

3. Results and discussion

$\gamma'-Fe_4N$ may be seen as a face-centered-cubic lattice of iron where $\frac{1}{4}$ of all octahedral sites are occupied by nitrogen in such a way that the octahedra are corner sharing. Two inequivalent iron sublattices can be accounted for. If we put N on the $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ position (Wyckoff 1b in the space group Pm3m) there is one type of iron at (0, 0, 0) (Wyckoff 1a) labelled Fe(I) and the three others, Fe(II) at $(\frac{1}{2},\frac{1}{2},0)$, $(\frac{1}{2},0,\frac{1}{2})$ and $(0,\frac{1}{2},\frac{1}{2})$ (Wyckoff 3c).

The electronic and magnetic structure of $\gamma'-Fe_4N$ have been elucidated for a long time [16] and numerous papers were published on magnetic nitrides [17,18]. From the spin-polarized densities of states (DOS, Fig. 1) three band regions could be distinguished. The lowest band is made up of the N 2p states strongly hybridized with the 3d–e_g orbitals of the Fe(II) atoms. Then the iron bands are located around the Fermi level with hardly any hybridization with nitrogen. These bands are occupied in the majority spin channel. About 10 electron volts above E_F the anti-bonding part of the p–d bands are located.

As a consequence of hybridization a strong covalent Fe(II)-N bond is observed and the resulting magnetic moment bearing by Fe(II) is low (lower than 2 μ_B). The bonding charge between Fe(I) and Fe(II) is weak as the distance is important and corner Fe(I) is rather isolated. Opposite to Fe(II) its magnetic moment is then higher than those of pure iron, around 3 μ_B. The coupling between the two iron sublattices is ferromagnetic (resulting magnetic moment around 9 μ_B) and all magnetic interactions have been analysed in the framework of the model of covalent magnetism [19].

Hydrogen atoms are put inside tetrahedrical vacant sites of the structure, i.e. $(0,0,\frac{1}{2})$, $(0,\frac{1}{2},0)$ and/or $(1/2,0,0)$ positions (Wyckoff 3d). These sites were occupied by empty spheres in our previous ASW calculations (ASA approximation) [16].

For pure $\gamma'-Fe_4N$ our equilibrium results are close to those found in literature (Table 1) [1,7,20]. As expected the insertion of hydrogen leads to an expansion of the cell and a decrease of the bulk modulus (Table 1 and Fig. 2).

Concerning the magnetization, a combined contribution of a magnetovolumic effect and a chemical bonding effect is observed. The first effect shrinks the 3d subbands of Fe and increases the 3d exchange splitting with the increase of unit cell volume. The second effect reduces local magnetic moments. In the case of $\gamma'-Fe_4NH$, the two effects compensate at equilibrium volume and the magnetization is nearly the same as for pure iron nitride, although the cell is expanded. Nevertheless the slope of the $M(V)$ curve is lower for Fe_4NH than for Fe_4N. Then for increasing hydrogen amounts ($n = 2, 3$) a drastic decrease of the total magnetization is observed. As the distances Fe(I)-H and Fe(II)-H are equal, hybridization effects are expected for either kind of iron. The corner Fe(I) atom is no longer isolated and strongly interacts

Table 1
Equilibrium properties of $\gamma'-Fe_4NH_n$, $n = 1, 2, 3$.

Phase	Fe_4N	$n = 1$	$n = 2$	$n = 3$
a (Å)	3.765	3.800	3.820	3.842
B_0 (GPa)	141	184	216	226
m_{av-SFP} (μ_B)	8.6	8.3	8.0	7.7
M (μ_B)	8.7	8.7	8.0	7.6
M (emu/g)	205	204	187	177

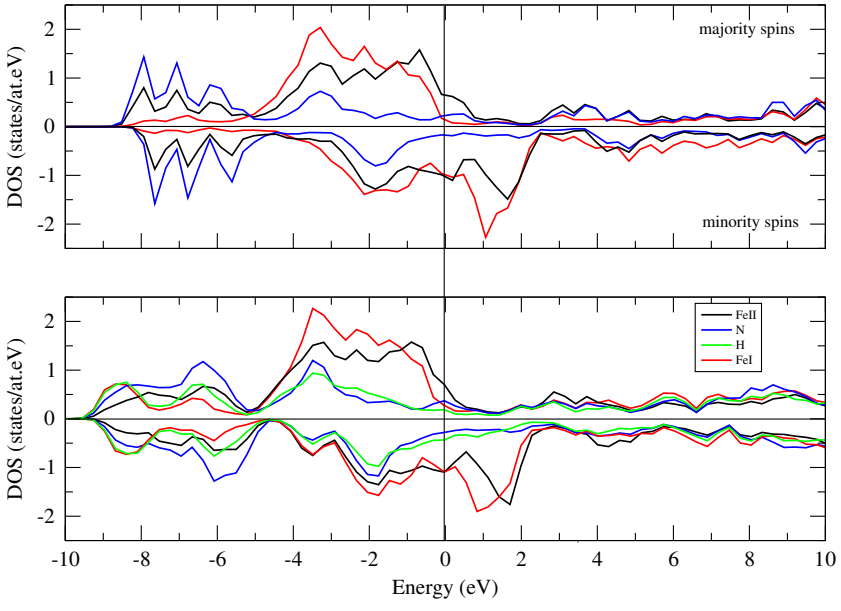

Fig. 1. Density of states for Fe_4N and Fe_4NH.