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Neutron diffraction study of the structural and magnetic properties of ε-$Fe_3N_{1.098}$ and ε-$Fe_{2.322}Co_{0.678}N_{0.888}$

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ABSTRACT

Binary ε-$Fe_3N_{1.098}$ and ternary ε-$Fe_{2.322}Co_{0.678}N_{0.888}$ were synthesized as spherical bulk materials using novel high-pressure solid-state metathesis reactions (HPSSM). The structural and magnetic properties of the two nitrides were investigated using neutron powder diffraction (NPD), a vibrating sample magnetometer (VSM), and first-principle calculations. We found that at high pressure and high temperature (HPHT), nitrogen atoms enter the interstitial 2d sites of the nitrogen-rich ε-$Fe_3N_{1.098}$ structure, space group $P6_322$, which were previously reported to be vacant. The stoichiometry of the nitride (N/Me ratio) and the level of disorder have a significant influence on the site occupancies and local magnetic moments in these iron-based nitrides. The substitution of Fe by Co in ε-$Fe_{2.322}Co_{0.678}N_{0.888}$ did not reduce the mean magnetic moment (μ_m) per metal atom at the Wyckoff 6 g site. NPD refinements showed that the magnetic moment per Fe atom in ε-$Fe_3N_{1.098}$ (at 1.8 (4) μ_B) was slightly higher than that of ε-$Fe_{2.322}Co_{0.678}N_{0.888}$, where the moment per Fe/Co atom is 1.7(2) μ_B.

1. Introduction

Iron-based nitrides have attracted enormous attention due to their potential applications in steel surface hardening, as corrosion-resistant materials, and as high-density magnetic recording media [1–3]. Binary iron nitrides form interstitial compounds containing variable amounts of nitrogen. The crystal structures of the α''-$Fe_{16}N_2$ and γ-$Fe_4N_{1+\delta}$ nitrides are derived from the body-centered cubic (bcc) α-Fe and face-centered cubic (fcc) γ-Fe structures, respectively [4,5]. Both ε-$Fe_3N_{1+\delta}$ and ζ-$Fe_2N_{1+\delta}$ are based on hexagonal-close-packed (hcp) ε-Fe [6–9]. Soft ferromagnetic ε-$Fe_3N_{1+\delta}$ form a homogenous solid solution over a broad range with δ varying from -0.40 to 0.48 [8]. In the ideal structure of ε-Fe_3N, crystallising with space group $P6_322$, the Fe atoms form a hcp arrangement with N atoms occupying one-third of the voids inside the Fe_6 octahedra in an ordered fashion (Fig. 1). Each Fe atom at the Wyckoff 6 g site is coordinated by two nearest-neighbor N atoms at the Wyckoff 2c site. The interstitial 2c site is the only available site for N atoms, with an occupancy factor equal to 1 ($occ._{2c} = 1$). The 2c octahedra share common vertices with each other, and share common edges and faces with 2b and 2d octahedra, respectively. In reality, however, the 2b site may also be occupied by N atoms ($occ._{2b} > 0$), with a resultant decrease in the ideal 2c site occupancy ($occ._{2c} < 1$) [8]. Previous studies indicate that the occupancy of the 2d site is always zero ($occ._{2d} = 0$) due to the N-N repulsive interactions, thus minimizing the configurational entropy [8]. However, it is not known whether the N atoms can occupy the interstitial 2d site, in a higher entropy configuration favoured by high temperature at high pressures (HPHT). On the other hand, metallic hcp ε-Fe, with a high intrinsic magnetic moment of 2.64 μ_B, does not exhibit magnetic ordering even at 0.03 K and 21.5 GPa [10]. However, the incorporation of interstitial N atoms can be expected to induce magnetic ordering in ε-Fe-based nitrides at higher temperatures, resulting in increased Curie

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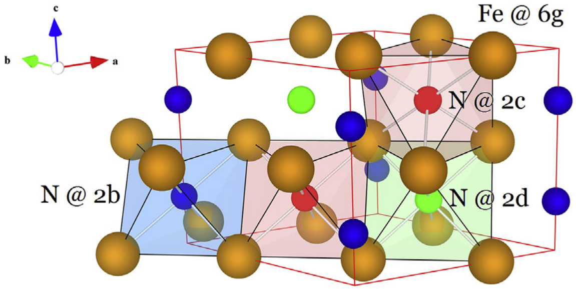

Fig. 1. Structure of ε-$Fe_3N_{1+\delta}$ in space group $P6_322$. Big yellow ball denotes the Fe atom at Wyckoff6g site; small red, blue, and green balls denote N atoms at 2c, 2b, and 2d sites, respectively. In idealε-$Fe_3N_{1+\delta}$, only the 2c position is occupied by N atoms. Diffusion of nitrogen results in the transfer of N atoms from 2c to 2b and 2d sites, suggesting an interstitial disordering process in nitrogen. In ternary ε-$Fe_{3\text{-}x}M_xN_{1+\delta}$, Fe atoms at 6 g site are partially substituted with Co/Ni atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

temperatures. Further investigations are therefore necessary to understand how the Fe magnetic moment is affected by the nitrogen content and site disordering in these materials. Stimulated by these open questions, we report, here, experiments aimed to elucidate the disordering of interstitial N atoms in hcp ε-Fe-based lattices.

Previous studies have described numerous attempts to modify or improve the structural and magnetic properties of Fe-based lattices by substituting Fe atoms with other transition metals in iron-based alloys [11–14]. Examples include ternary ε-$Fe_{3\text{-}x}Co_xN_{1+\delta}$ alloys, which are isostructural to hexagonal ε-Fe_3N. The Fe and Co atoms sit at Wyckoff 6 g sites and the N atoms sit in interstitial voids formed by Fe_6 octahedra, typically in a disordered arrangement. Atomic disordering significantly affects the chemical bonding state and magnetic moments of these alloys. In the hcp ε-Co structure the Co atom (1.64 μ_B) possesses a lower magnetic moment than Fe in hcp ε-Fe (2.64 μ_B). However, the substitution of Fe by Co does not directly reduce the mean magnetic moment [14]. In ternary alloys, since Co randomly replaces Fe, an exchange interaction exists between the Fe 3d, Co 3d, and N 2p states, which may induce localized spin effects or the appearance of long-range ferromagnetic ordering.

Neutron powder diffraction (NPD) is a unique and powerful method for precisely determining the atomic occupancy at sites as well as magnetic structures. We report, here, the results of NPD experimental and first-principles calculations on binary ε-$Fe_3N_{1.098}$ and ternary ε-$Fe_{2.322}Co_{0.678}N_{0.888}$ nitrides. The primary motivation for this work was to further probe the effects of interstitial elements and substitution disordering on the structural and magnetic properties of iron-based nitrides.

2. Experimental and theoretical calculations

The incorporation of nitrogen into the crystalline structure of a metal alloy is often thermodynamically unfavorable. High-pressure thermodynamically favors the formation of highly crystalline iron-based nitride materials via a high-pressure solid-state metathesis (HPSSM) reaction [15]. The HPSSM reaction is an effective method of synthesizing metal nitrides, such as GaN, CrN, VN, Re_3N, and MoN_2 [16–21]. In this study, binary ε-$Fe_3N_{1+\delta}$ and ternary ε-$Fe_{3\text{-}x}Co_xN_{1+\delta}$ were prepared via HPSSM synthesis routes. Hexagonal boron nitride (*h*BN), Fe_2O_3, and Co_2O_3 were used as reaction precursors. The chemical reaction equations can be described as:

$$3Fe_2O_3+6BN \rightarrow 2Fe_3N + 3B_2O_3 + 2N_2 \quad (1)$$

$$(3\text{-}x)Fe_2O_3+xCo_2O_3+6BN \rightarrow 2Fe_{3\text{-}x}Co_xN+3B_2O_3+2N_2 \quad (2)$$

The reaction precursors were compressed to 5 GPa, heated to 1673 K for 3 min, and quenched to room temperature in 1 min with a subsequent release of pressure. The detailed experimental procedures are described elsewhere [22,23]. High-pressure chemical reactions play an important role in the design of our novel material synthesis. The higher reactivity of oxygen with respect to nitrogen means that care has to be taken to prevent the formation of oxides. Our high-pressure confining environment allows nitrogen to take part in the chemical reaction unhindered by the competition with oxygen. In HPSSM reactions, B atoms tend to bond with O atoms to form borates, which typically have lower formation enthalpies as compared to boron diffusion into the metal interstitial sites to form metal borides [15]. A metallic spherical bulk iron-based nitride with a diameter of ~5 mm was formed in the center of the recovered high-pressure assembly. After mechanical separation, the spherical products were washed in distilled water and alcohol with an ultrasonic washer to remove any residues. Fig. 2a shows three such as-synthesized magnetically-ordered iron-based nitride samples.

The as-synthesized iron-based nitride samples were first investigated by field-emission scanning electronic microscopy (FE-SEM, JSM-7000 F, JEOL) and X-ray powder diffraction (XPD) with Cu *Kα* radiation (Fangyuan, DX-2500). The SEM image (Fig. 2b) demonstrates that nitrogen-degassing in the HPSSM reactions gave rise to abundant cavities inside the nitride products. The XPD patterns (Fig. 3) indicate that the binary and ternary nitrides were highly crystalline. The approximate atomic ratios were determined by energy dispersive X-ray spectroscopy (EDX), and then used in further NPD refinements. For EDX quantitative analyses, well-polished iron-based nitride samples and EDX standard samples (pure-phase Fe, Co, and *h*BN) were uniformly coated with an osmium layer (5 nm thick) in an osmium coater (Neoc-STB, Meiwafosis Co., Ltd). An EDX detector (Oxford Instruments, INCA E250) installed on a field-emission scanning electronic microscope (FE-SEM, JSM-7000 F, JEOL) was used for quantitative EDX analyses. The EDX method used in this study can effectively quantify the content of light and heavy elements (such as Fe, Co, and N). The accuracy of the quantification was evaluated to not be less than 0.5% [24,25]. Hysteresis loops were measured under a field of up to 21,000 Oe in a vibrating sample magnetometer (VSM, MicroSense-VSM-EV9) to analyze the magnetic properties.

The NPD experiments were carried out at room temperature using the neutron powder diffractometer of the Institute of Nuclear Physics and Chemistry, P.R. China. Approximately 3 g of each pure-phase iron-based nitride sample in powdered form, obtained from 12 high-pressure runs, was placed into a thin-walled vanadium can (6 mm in diameter). NPD data were collected at a wavelength of $\lambda = 1.57$ Å over the range of $2\theta = 20–140°$ with a step of 0.1°/s. The counting time was 10 h with a neutron flux of 3×10^5 n cm^{-2} s^{-1} at the sample position. The data were refined using FULLPROF SUITE ver.1.10 Rietveld refinement software. Two possible space groups ($P6_322$ and $P312$) were used for structural NPD refinements. For the space group $P6_322$, reliability factors of the refinements were $R_{wp} = 9.70$ and $\chi^2 = 2.36$ for ε-Fe_3N, and $R_{wp} = 6.92$ and $\chi^2 = 1.60$ for ε-Fe_2CoN. When using $P312$, reliability factors of the refinements were higher, $R_{wp} = 11.10$ and $\chi^2 = 3.16$ for ε-Fe_3N, and $R_{wp} = 7.77$ and $\chi^2 = 2.01$ for ε-Fe_2CoN. Therefore, we selected a more reasonable space group, $P6_322$, for structural and magnetic structure description. Neutron scattering lengths are $b(\text{Fe}) = 0.954 \times 10^{-12}$ cm, $b(\text{N}) = 0.936 \times 10^{-12}$ cm, and $b(\text{Co}) = 0.253 \times 10^{-12}$ cm [8,26]. There is a large difference in neutron scattering length between Fe and Co, and therefore a significant difference in the intensity of the neutron diffraction peaks