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Iron nanoparticles with tunable tetragonal structure and magnetic properties

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Abstract

Body-centered cubic (bcc) Fe is known as a typical soft magnetic material with high saturation magnetization ($M_s$) and low magnetocrystalline anisotropy. However, first principle calculations demonstrate that body-centered tetragonal (bct) Fe has higher magnetocrystalline anisotropy and comparable $M_s$ with bcc Fe. In this work, bct Fe nanoparticles (NPs) were successfully fabricated by a gas-phase condensation method for the first time. The bct Fe phase is confirmed by X-ray diffraction pattern and diffraction images of transmission electron microscopy. An increased magnetocrystalline anisotropy of bct Fe, $(2.65\pm0.67)\times10^5$ J/m$^3$ ($(21.2\pm5.3)$ µeV/atom), is observed, which is around seven times higher than that of bcc Fe $4.8\times10^4$ J/m$^3$ (3.5 µeV/atom). The bct Fe NPs sample has coercivity of $3.22\times10^5$ A/m at 5 K and $1.04\times10^5$ A/m at 300 K, which are much higher than that of bcc Fe NPs. In addition, the saturation magnetization at 5 K is estimated to be $(1.6 \pm 0.4) \times10^6$ A/m $(2.2 \pm 0.5$ μB/atom), comparable to that of bcc Fe $1.7 \times10^6$ A/m $(2.2$ μB/atom).

Keywords: magnetic nanoparticle, body-centered tetragonal Fe, magnetocrystalline anisotropy, gas-phase condensation
I. Introduction

Magnetic nanoparticles (NPs) that possess a large maximum energy product, \((BH)_{\text{max}}\), have attracted significant attention for their application in permanent magnets (PMs) technologies, like electric motors [1] and wind turbines. [2] Therefore, materials with large magnetic anisotropy energy (MAE) and high saturation magnetization \((M_s)\) are good candidates for PMs. Rare-earth (RE) PMs have good magnetic performance and thermal stability. However, the socioeconomic supply limitations and high price of RE elements, such as neodymium and dysprosium, stimulate new research on alternative magnetic materials. [3,4] Therefore, new magnetic materials for PMs should be inexpensive and naturally abundant. Current research aims to enhance the MAE in materials that already possess large \(M_s\) using structural asymmetry like tetragonal distortion. One such example is the tetragonal \(L_{10}\) phase FePt. [5,6] Despite its suitable magnetic properties, precious metal Pt is not cost-effective for broad use. Fe known as a soft magnetic material is attractive because of its small MAE \(4.8\times10^4 \text{ J/m}^3\), [6] high \(M_s\), and abundant availability on the earth. Even higher \(M_s\) of Fe with the metastable \(Fe_6\) phase was reported. [8] Fe should have high magnetic coercivity to obtain large \((BH)_{\text{max}}\). In 2004, Burkert et al. predicted the MAE of tetragonal Fe and FeCo could increase by orders of magnitude, while the \(M_s\) is still close to bcc Fe and bcc FeCo. [9,10] Therefore, combing high \(M_s\) and large MAE, bct Fe is a promising candidate for non-rare-earth PMs.

Research on tetragonal Fe firstly focuses on ultra-thin films to investigate the structural and magnetic properties. [11–15] Martin et al. point out Fe monolayers on Ir(001) showing thickness-dependent structure properties, where 2 monolayers Fe has face-centered tetragonal (fct) structure and body-centered tetragonal (bct) structure for 3-10 monolayers Fe. [16]
However, no experimental results report large MAE of bct Fe. However, experimental results on bct FeCo thin film and core-shell nanoparticles (bct FeCo shell with AuCu core) indicate that bct FeCo has high MAE and $M_s$, which are consistent with theoretical predictions.\cite{17,18}

Experimental investigation of bct Fe and FeCo are on strained thin films or strained core-shell structures. Thus, the strong demagnetization field may conceal the MAE, which may hinder the further characterization and understanding of those new materials. As a result, NPs samples with single magnetic domain are desirable for both fundamental magnetic research and technological applications such as PMs.

In order to prepare bct Fe NPs, Fe phase diagram is investigated at first. According to the low pressure phase diagram of pure Fe,\cite{19} face-centered cubic (fcc) $\gamma$-Fe is stable at high temperatures (between 910 °C and 1394 °C) and bcc $\alpha$-Fe at low temperatures (below 910 °C). Compared to bcc $\alpha$-Fe, fcc $\gamma$-Fe can be treated as a distorted bcc $\alpha$-Fe with a c axis stretched to $c/a = \sqrt{2}$. Therefore, according to the Bain path, a metastable bct Fe should exist as an intermediate phase between fcc $\gamma$-Fe and bcc $\alpha$-Fe.\cite{20} In our gas-phase condensation (GPC) method, the NPs always evolve from a high temperature phase to a low temperature phase due to the plasma heating effects.\cite{21,22} In order to get the intermediate bct Fe, Fe NPs need to be quenched at the intermediate stage before they evolve into the stable bcc phase. Therefore, properly controlled quenching is a critical requirement to prepare bct Fe NPs.

In this work, bct Fe NPs were prepared for the first time by a GPC system. The plasma heating effect of the GPC system is modulated by sputter current, magnetic field, and gas flow rate to achieve a proper quenching requirement for the formation of bct Fe. The bct Fe NPs exhibit a magnetic coercivity of $3.22 \times 10^5$ A/m at 5 K and $1.04 \times 10^5$ A/m at 300 K and MAE≈$(2.65\pm0.67)\times10^5$ J/m$^3$ ($(21.2\pm5.3)$ µeV/atom) with comparable $M_s$ with bcc Fe.
II. Experimental Details

Fe NPs were synthesized using a magnetron-sputtering-based gas-phase condensation (GPC) system. The GPC system was shown in figure 1, containing a source chamber and a deposition chamber connected by a small aperture. 2” high purity Fe planer target (99.95 %) was used to fabricate Fe NPs. In order to prepare NPs, a much higher sputtering pressure (350 mTorr) is used. [23,24] Such a high sputtering pressure could greatly increase the collision rate between the sputtered atoms and Ar atoms, and the energy of the sputtered atoms transfers to Ar atoms and then the sputtered atoms are cool down following with NP nucleation and growth. [25,26] During the fabrication process, the sputtering current was varied from 0.2 A to 0.6 A. The pressure in the source chamber was kept as 350 mTorr by ultrahigh purity argon gas, while the pressure in the deposition chamber was below 1 mTorr to create a pressure differential between source chamber and deposition chamber. Due to this pressure differential, an argon gas flow was formed from the source chamber to the deposition chamber. The synthesized Fe NPs were carried by argon gas flow to the deposition chamber. The NPs were deposited onto two different kind of substrates: amorphous carbon-coated Cu grid and single crystal Si wafer. A Ti capping layer was deposited onto Fe NPs collected on Si substrate to protect Fe NPs from oxidation. However, no capping layer was deposited for Fe NPs collected on Cu grid which was used for transmission electron microscopy (TEM) characterization.

In order to control the growth and phase formation of Fe NPs, field-controlled plasma-heating effects were promoted. As shown in figure 1, magnetic field intensity was modified by varying Cu disk thickness behind the Fe target. The magnetic field distribution was adjusted by Fe ring and cone. [27,28] In our GPC system, NPs are formed from a high temperature phase to
a low temperature phase following the thermal gradient induced by plasma. The plasma region depends on sputtering current $I$ and magnetic field intensity $B$. Different $I$ and $B$ could form longer or shorter plasma regions as shown figure 1. In the case of a high current and small magnetic field, plasma region is long because of the higher cathode accelerating voltage and less plasma confinement from small magnetic field (dash line in figure 1). In contrary, low current and large magnetic field could induce short plasma region (solid line in figure 1). At the edge of plasma region (black solid line and dash line in figure 1), Fe NPs quench down dramatically due to the lack of energy source. It means that the plasma boundary behaves as the quench boundary for Fe NPs. By changing the current and magnetic field, the plasma region stretches back and forth. Accordingly, Fe NPs can quench at a certain intermediate phase like bct phase. As shown in figure 1, under the condition high current and small magnetic field ($I_1$, $B_1$), the plasma region is long and Fe NPs have more time to gradually cool to the bcc Fe phase. While low current and high magnetic field ($I_2$, $B_2$) are applied, bct Fe NPs start to form. In this paper, bcc Fe NPs were prepared using $I_1 = 0.6$ A and $B_1 = 700$ G and bct Fe NPs were obtained using $I_2 = 0.2$ A and $B_2 = 850$ G.

Several characterization methods were used to investigate the phase information, morphology, and magnetic properties of Fe NPs. The phase of Fe NPs was characterized by XRD and high resolution transmission electron microscopy (HRTEM). Convergent-beam electron diffraction (CBED) imaging technique was used to further confirm the phase information. Elemental analysis was performed by scanning TEM energy dispersive X-ray spectroscopy (STEM-EDS). Magnetic hysteresis loops measurements were done by a magnetic properties measurement system (MPMS) at temperature ranging from 5 K to 300 K.
Figure 1. Schematic diagram of Fe nanoparticle synthesis system, integrated with the illustration for the concept of tuning the thermal history for the growth of bcc and bct Fe nanoparticles. Letting the sputtering current $I_1 > I_2$ and the surface magnetic field at the target $B_1 < B_2$, the plasma region is longer for $(I_1, B_1)$ than for $(I_2, B_2)$ resulting in two different spatial quenching boundaries shown as a dotted line and a solid line respectively. Varying $I$ and $B$, different phases of Fe NPs can be obtained.

III. Results and Discussion

A. Structure and morphology analysis

In order to get the evidence of tetragonal distorted phase of Fe NPs, XRD pattern is collected as shown in figure 2. Three diffraction peaks with approximately equal proportions centered around the bcc Fe (110), are observed. These adjacent peaks match well with bcc Fe and tetragonal distorted bcc Fe phase. CrystalMaker software is used to simulate diffraction
patterns for bcc and bct Fe. A bcc Fe structure is simulated using a standard database as a control pattern. And a bct Fe structure is also simulated using lattice constants of $a = 2.75 \, \text{Å}$ and $c = 3.38 \, \text{Å}$ ($c/a = 1.23$), determined from the XRD pattern assuming a tetragonal crystal structure. The simulated diffraction peaks match well with the experimental data, indicating that the sample contains bct Fe phase. From the XRD pattern, some bcc Fe NPs still exist in the Fe NPs sample, which is due to the inhomogeneous quenching effects along the etching track of Fe target. The diffraction peak around 2 theta 69 degree is from the Si substrate. Small diffraction peaks around 48 and 49 degrees originate from the oxidation of capping layer. Moreover, no iron oxide diffraction peaks are observed. Phase characterizations of bcc Fe NPs sample is in the supplemental materials. [29]
Figure 2. XRD patterns of Fe NPs formed at I₂ = 0.2 A and B₂ = 850 G. The black line, blue line, and red line are the diffraction pattern of experimental results, simulated bct Fe diffraction peaks, and simulated bcc Fe peaks respectively.

In order to obtain further information on bct Fe NPs, the morphology and structure of the Fe NPs are investigated using HRTEM operated at 300 keV for bright-field imaging and diffraction patterns are operated at 100 keV (to mitigate beam damage on NPs) for the CBED imaging. The size distribution of NPs is estimated using TEM with lower magnification. The size of NPs follows Gaussian distribution with 12 nm average size and 2.6 nm standard deviation. Both polyhedral and cubic NPs are found as shown in figure 3(a). The cubic NPs are to be bcc Fe and more information is in the supplemental materials. [29] The crystallinity of polyhedral particles is demonstrated by high-resolution bright-field imaging as shown in figure 3(b), where a shell of the Fe NP is observed due to the oxidation of Fe NPs (see elemental analysis in supplemental materials [29]). Indexing the core lattice fringes is done by comparing the fast-Fourier transform (FFT) of the region within the red box to a diffraction pattern simulated by CrystalMaker software. The forbidden peaks in FFT are also accounted for during the comparison. The standard method of indexing these patterns is done by comparing diffraction vector ratios, \( g_1/g_2 \), and angles, \( \theta \), with those of known phases and orientations. The ratio and angles shown in figure 3 (c) match poorly with a bcc structure so they are compared with a bct structure simulated with lattice constants determined from the XRD pattern. The FFT pattern is matched well with a [131] zone axis pattern of the bct Fe structure. To further characterize the polyhedral particles, CBED analysis is carried out on a single polyhedral NP, as shown in figure 3(d). The CBED pattern is compared with the simulated diffraction pattern of bcc Fe structure. Again, no diffraction ratios or angles of the bcc structure match with the experimental CBED
pattern. A main feature of the CBED pattern is that the angle between diffraction peaks is not 90 degree, as would be expected for a bcc Fe. The simulated bct structure determined from XRD pattern, not shown here, matches better with the CBED pattern than the bcc structure. However, it is still not within the error of our measurements. The deviation of our simulated bct pattern based on the XRD results can be understood by considering the non-uniformity of the Fe NPs. Certain NPs may have different lattice constants depending on their local strain. To improve our simulated bct Fe diffraction pattern, the experimental lattice constants are calculated directly from the CBED pattern shown in figure 3(d). The new diffraction pattern simulated using these calculated values is shown in figure 3(f). As shown in figure 3(e,f), the NP CBED pattern shown in figure 3 (d) is not consistent with a bcc Fe structure; however, good agreement is achieved assuming a bct Fe structure.
Figure 3. TEM images of Fe NPs formed by GPC, (a) Bright-field image of polyhedral and cubic Fe NPs, (b) HRTEM image of polyhedral Fe NPs, (c) FFT of the red square in (b) (where $g_1$, $g_2$, and $\theta$ are two diffraction vectors and the angle between them respectively). (d) Convergent beam electron diffraction (CBED) pattern of a single polyhedral Fe NP, (e) and (f) are simulated diffraction patterns for bcc and bct Fe crystal structures.

B. Magnetic characterization

Hysteresis loops are measured to demonstrate the high MAE of bct Fe NPs. Magnetic in-plane (IP) and out-of-plane (OP) hysteresis loops of bct Fe NPs sample are shown in figure 4 (a) and (b) respectively. Applied magnetic field is parallel to substrate for IP loops and perpendicular for OP loops. IP loops show that bct Fe NPs sample has coercivity of $1.04 \times 10^5$ A/m at 300 K and $3.22 \times 10^5$ A/m at 5 K. As an experiment control, bcc Fe NPs sample is also prepared and the coercivity of bcc Fe NPs sample is $0.60 \times 10^5$ A/m at 300 K and $0.96 \times 10^5$ A/m at 5 K as shown in figure 4(c). From the TEM images shown in figure 3(a), Fe NPs have in-plane chain structures, which may enhance the coercivity of IP loops.[21,22] Therefore, OP loops are also measured to differentiate shape anisotropy from magnetocrystalline anisotropy. As shown in figure 4(b), OP loops have coercivity of $0.92 \times 10^5$ A/m at 300 K and $2.74 \times 10^5$ A/m at 5 K, which are both slightly smaller than that of IP loops. OP hysteresis loops of bcc Fe NPs sample are also measured with coercivity $0.42 \times 10^5$ A/m at 300 K and $0.73 \times 10^5$ A/m at 5 K as shown in figure 4(d). bct Fe NPs sample shows higher coercivity for both IP and OP loops than that of bcc Fe NPs, indicating bct Fe NPs has higher MAE. Although NP chains can increase the coercivity slightly, the main reason for the high coercivity of bct Fe NPs sample is due to high magnetocrystalline anisotropy from the tetragonal phase.
The $M_s$ of bct Fe NPs sample could be estimated using the hysteresis loops measured by MPMS and TEM images, which allow to obtain the magnetic moment and NPs volume of the sample, respectively. The NPs coverage ratio on the silicon substrate is assumed to be the same as that for the TEM sample. Therefore, the total volume of NPs is estimated using the coverage ratio, the mean size of NPs, and the area of silicon substrate. Using these assumptions, the $M_s$ of bct Fe at 5 K is $(1.6 \pm 0.4) \times 10^6$ A/m $(2.2 \pm 0.5 \, \mu_B$/atom). The error bar for $M_s$ is from the size and the coverage ratio variation of NPs. The $M_s$ of bcc Fe is also estimated using the same method and the mean value of $M_s$ is similar as bct Fe NPs sample.

The ratio of bct/bcc Fe could also be estimated using 5 K IP hysteresis loops shown in figure 4. Small kinks are in the second quadrant with $M/M_s$ ranging from 0.52 to 0.18. The kinks indicate there are two phases in the sample, bcc and bct Fe. bct Fe shows higher coercivity compared to bcc Fe. Since the $M_s$ of bcc Fe and bct Fe are similar, the bct Fe phase ratio could be estimated in a range between 46 % to 84 % (see supplemental materials [29]).
The magnetocrystalline anisotropy $K_u$ of bct Fe NPs sample is estimated by its temperature dependent coercivities. Hysteresis loops are measured at temperatures ranging from 5 K to 300 K. Coercivity decreases as the temperature increase due to thermal fluctuation. $K_u$ could be derived from Sharrock equation using temperature dependent coercivities. [31,32]

$$H_c(T) = H_0 - H_0 \left[ \frac{k_B}{K_u V} \ln(f_0 T) \right]^{\frac{2}{3}} T^{\frac{2}{3}}$$  \hspace{1cm} (1)

Where $H_c(T)$ represents coercivity at different temperature, $H_0$ is the coercivity at 0 K, $k_B$ is Boltzmann’s constant, $V$ is the volume of the bct phase NP, $f_0$ is the attempt frequency $\sim 10^9$ Hz,
and t is the measure time (~5 sec). Here the exponent 2/3 is used for Sharrock equation due to the magnetic interactions and easy axes distribution of NPs. Figure 5 shows the experimental data and fitting curve based on equation (1) and the fitting result matches experimental data very well. Based on the linear relationship between coercivity and $T^{2/3}$, $K_uV$ is estimated as $\sim 1.63 \times 10^{-19}$ J. Since the size of NPs is smaller than 100 nm as shown in figure 3, Sherrer equation is used to estimate the average grain size of bct Fe NPs using XRD pattern shown in figure 2. [33] The bct Fe crystal size is ranging from 9.8 nm to 11.6 nm. Therefore, the magnetocrystalline anisotropy could be estimated as $K_u \sim (2.65\pm0.67) \times 10^5$ J/m$^3$ $((21.2\pm5.3)$ $\mu$eV/atom), which is around seven times higher than that of bcc Fe $4.8 \times 10^4$ J/m$^3$ (3.5 $\mu$eV/atom).

![Figure 5](image.png)

Figure 5. Temperature dependent coercivity of bct Fe NPs sample, where black squares stand for experimental data and red dash line is the fitting curve based on equation (1).
IV. Conclusions

In conclusion, polyhedral Fe NPs with large coercivity and high saturation magnetization have been successfully synthesized by a GPC method. The large coercivity is attributed to a strain-induced tetragonal bct Fe phase, which has higher magnetocrystalline anisotropy compared with bcc Fe. Initial XRD characterization shows a peak splitting which is consistent with a tetragonal distortion of bcc Fe. High resolution TEM lattice fringe indexing and CBED pattern analysis also demonstrate the bct phase of these NPs. With this evidence, it is hypothesized that these polyhedral Fe NPs are the first experimental demonstration of the metastable bct Fe phase predicted by first principle calculations. Future work will further confirm the absolute lattice constants and phase of these NPs as well as more comprehensively determine how the NP size, NP interaction and strain effects on the magnetic properties of the NPs. This work proves the feasibility for the formation of highly strained polyhedral Fe NPs which are promising candidates for future non-rare-earth permanent magnetic materials.

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Author contributions

Jinming Liu, Shi-Hai He and Jian-Ping Wang designed the experiment. Jinming Liu and Shi-Hai He fabricated the sample and measured the XRD, TEM, and hysteresis loops. Karl Schliep performed the HRTEM, CBED, and STEM characterization and contributed to the Fe phase analysis and the manuscript preparation. David Flannigan contributed to the TEM analysis. Bin Ma contributed to the data analysis. Ying Jing did part of the NP sample synthesis and analysis. Jian-Ping Wang initialized and coordinated the whole project. Jinming Liu and Jian-Ping Wang drafted the manuscript and all co-authors commented on the manuscript.

References:


[29] See Supplemental Material at… for the detailed description of phase characterization of bcc Fe NPs, elements analysis of bct Fe NPs, bct Fe phase ratio calculation, and $K_u$ estimation.


