Double-Layer Hexagonal Fe Nanocrystals and Magnetism

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A high-pressure phase of iron, double-layer hexagonal close-packed (DHCP) structure, is observed upon pulsed-laser ablation of an iron target in liquid under the conditions of room temperature and ambient pressure, and meanwhile DHCP iron nanocrystals with 10–20 nm diameter are prepared. The magnetism measurements of the prepared nanocrystals indicate that DHCP iron nanocrystals are nonferromagnetic. The stability of DHCP iron nanocrystals under normal temperature and pressure is attributed to the nanosized confinement effect of nanocrystals.

I. Introduction

A variety of iron structures as well as their applications in optoelectronics and magnetism have been attracting many research interests. Many kinds of iron-based nanomaterials such as single iron, iron oxide, and alloy have been prepared by several methods.[1–9] For instance, some metastable phases of iron have been prepared in multilayer films by molecule beam epitaxy (MBE).[10–14] Interestingly, Mao et al.[15] observed a metastable phase of iron called double-layer hexagonal close-packed (DHCP) by synchrotron X-ray diffraction experiment in a diamond-anvil cell system, which suggested that, besides the ϵ (HCP) iron, the DHCP iron may be one of the high-pressure phases of iron in the earth's core. However, there have not been any studies showing the DHCP iron could exist under the conditions of room temperature and ambient pressure.[15,16] Recently, we have developed a laser-basis technique to prepare nanomaterials and nanostructures with metastable phases, i.e., pulsed-laser-induced liquid–solid interface reaction (PLIIR).[17] In this contribution, we report that the DHCP phase of iron is observed upon pulsed-laser ablation of an iron target in liquid, while DHCP nanocrystals of iron are prepared using PLIIR. Additionally, the magnetic property of the prepared nanocrystals is characterized by a superconducting quantum interference device (SQUID), showing that DHCP nanocrystals of iron seem nonferromagnetic. Importantly, our studies demonstrate that the metastable phase that does not exist in bulk under normal conditions may be stable in nanocrystals due to the nanosized confinement effect.[18]

II. Experimental Section

The PLIIR preparation of DHCP nanocrystals of iron in our study is as follows. The second harmonic is produced by a Q-switch neodymium-doped yttrium aluminum garnet laser device with wavelength of 532 nm, pulse width of 10 ns, repeating frequency of 5 Hz, and pulse energy of 20 mJ. In our experiment, the $FeCl_2$ solution with 1 mM is used as the reactive liquid and the solid target is a single iron bulk (99.97%). The iron target is first fixed on the bottom of a reactive chamber. Then, the solution is poured slowly into the chamber until the target is covered by 5 mm. Finally, the pulsed laser is focused onto the target surface. During the laser ablating, the target and solution are maintained at room temperature. Meanwhile, the target rotates at a slow speed (10 rpm). After the pulsed laser interacted with the target for 30 min, the powders are collected from the solution, which are the samples to be analyzed in our case. A scanning electron microscope (SEM), X-ray diffraction (XRD), a micro-Raman spectrometer, and a transmission electron microscope (TEM, JEOL2010, 200 kV, operating with Digital Micrograph 1.0.0.8) equipped with an energy depressive X-ray spectrometer (EDS) within the measuring error of 2% are

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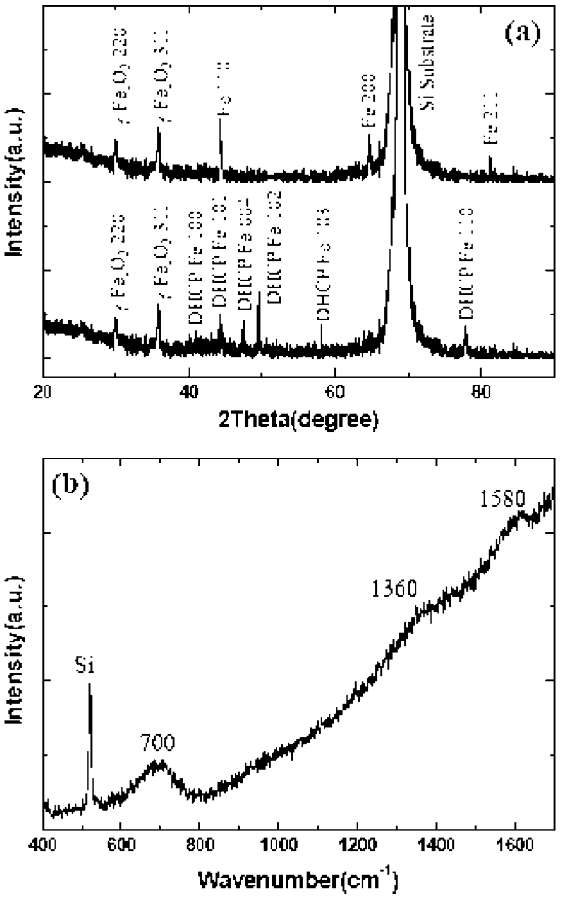

Figure 1. (a) XRD pattern of the original as-synthesized sample (lower curve) and the same sample stored for 6 months (the upper curve). (b) Raman spectrum of the sample.

employed to determine the morphology, structure, and composition of the as-prepared sample upon PLIIR.

III. Results and Discussion

Figure 1 shows the XRD pattern and Raman spectrum of the sample. Definitely, the (100), (101), (004), (102), and (103) character peaks of the DHCP phase of iron are observed according to JCPDS in Figure 1a.[19] This result indicates that the DHCP phase of iron forms upon PLIIR above. Meanwhile, two character peaks of γ-Fe_2O_3 are observed.[20] In Figure 1b, the broad peak around 700 cm^{-1} and the two peaks at 1360 and 1580 cm^{-1} are attributed to γ-Fe_2O_3,[4,21] and the strong peak at 520 cm^{-1} is due to the signal of Si substrate. Therefore, these results show that the sample is a mixture of DHCP iron and γ-Fe_2O_3. Another XRD measurement is taken to the same sample stored for about 6 months, as shown in the upper curve of Figure 1a. Interestingly, the DHCP Fe signal disappears, and the normal cubic Fe phase appears instead.[22] This result definitely displays a time-resolved lattice relaxation of the sample, which induces the phase transition from the metastable high-pressure phase to the stable normal phase. Accordingly, the prepared DHCP phase of iron is a metastable structure under the conditions of room temperature and ambient pressure.

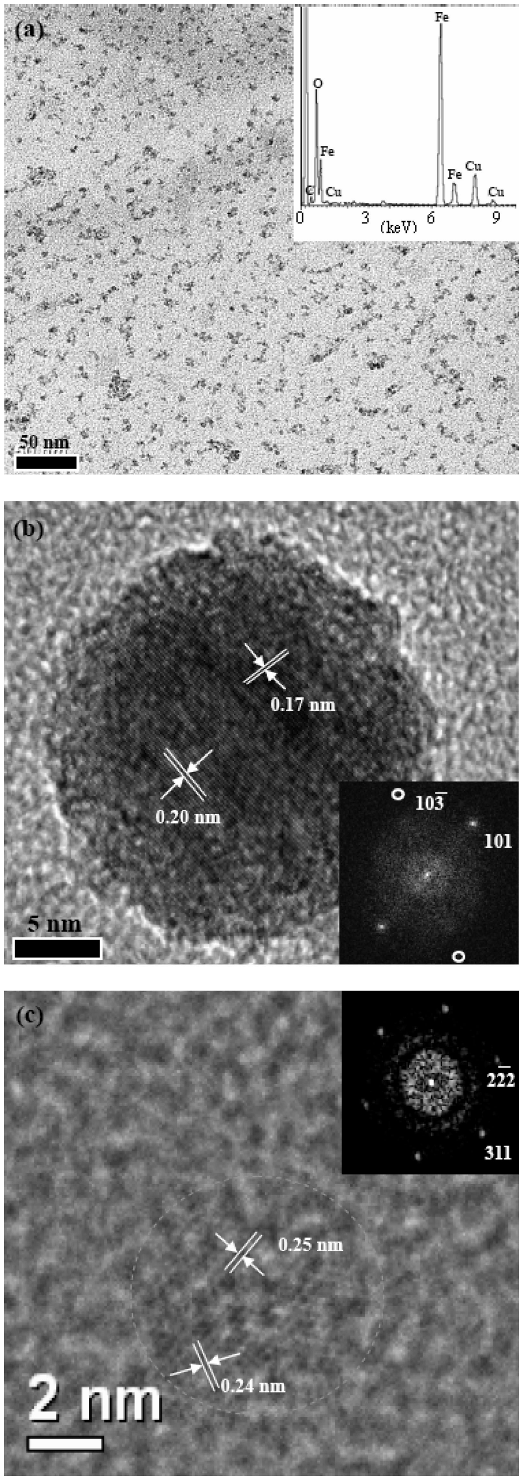

Figure 2. (a) Low-magnification TEM image and the corresponding EDS (inset). (b) HRTEM image of a DHCP nanocrystal of iron and the corresponding SAD pattern (inset) by fast Fourier transform (FFT). (c) HRTEM image of a γ-Fe_2O_3 nanocrystal and the corresponding SAD pattern (inset) by FFT.

Figure 2a shows the TEM bright-field image with low magnification of the as-prepared sample. Clearly, the prepared sample is nanocrystal, and the shape of nanocrystals is spherical and the size is in the range 2−20 nm. EDS of the sample shows 40.1% atoms are Fe and 28.0% are oxygen while carbon and copper are from the amorphous carbon hold film and the copper grid in the TEM specimen (inset in

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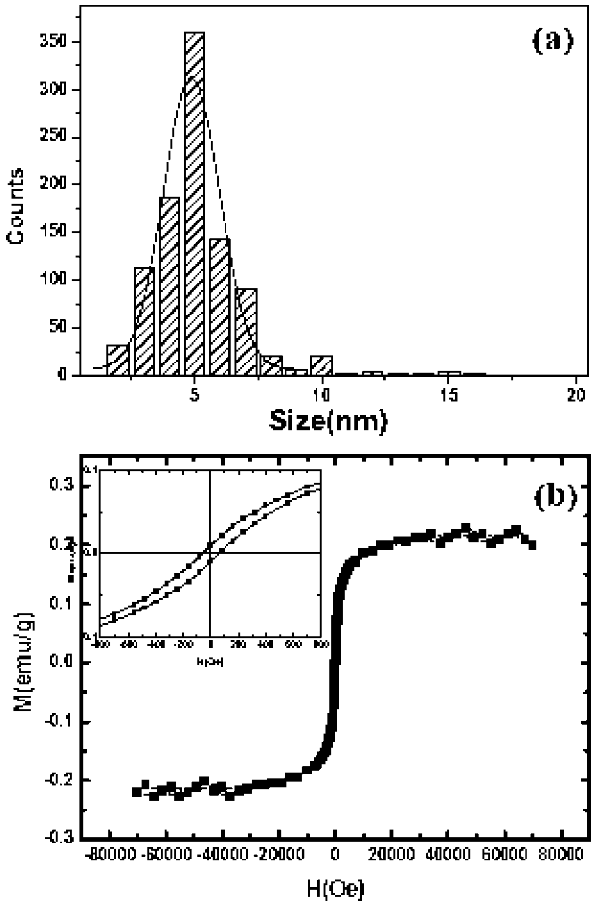

Figure 3. (a) Size distribution of nanocrystals summarized from Figure 1a. (b) Magnetic property of nanocrystals by SQUID, while $H_s = 0.2$ emu/g and $H_c = 62$ Oe.

Figure 1a). Further, Figure 2b shows the high-resolution TEM (HRTEM) image of a DHCP nanocrystal of iron, and the corresponding selected area electronic diffraction (SAD) pattern is shown in the inset of Figure 2b. The HRTEM pattern shows that the interplanar spacing of 0.20 and 0.17 nm are corresponding to the crystallographic planes of (101) and (103) of DHCP iron, respectively. The SAD pattern is identified to be the DHCP phase of iron crystal. In addition, the HRTEM image of γ-Fe_2O_3 nanocrystals is shown in Figure 2c. The interplanar spacing of 0.25 and 0.24 nm are corresponding to the crystallographic planes of (311) and (222) of γ-Fe_2O_3, and the SAD pattern shown in the inset in Figure 2c is identified to be γ-Fe_2O_3. Therefore, these experimental data show that the both DHCP phase of iron and γ-Fe_2O_3 nanocrystals are prepared by PLIIR.

Based on the statistics of TEM, the size distribution of the prepared nanocrystals is summarized in Figure 3a. By carefully identifying in TEM, we find that the mean size of γ-Fe_2O_3 nanocrystals is about 5 nm in diameter, and there are some big ones that are smaller than 10 nm. Then, the mean size of DHCP nanocrystals is about 10 nm in diameter, and there are some big ones that are smaller than 20 nm in diameter. Therefore, γ-Fe_2O_3 nanocrystals are the majority in the as-prepared sample. SQUID is employed to measure the magnetic property of the sample at room temperature. Figure 3b shows the hysteresis loop of the sample. The saturated magnetization is about 0.2 emu/g, and the coercivity is about 60 Oe. As is well known, the saturated magnetization of γ-Fe_2O_3 is usually in the range 1−70 emu/g.[1,4,5,23] However, the magnetism of nanocrystals will decay with the surface-to-volume atoms ratio (S/V) increasing because the surface phase breaks the symmetry compared with the inner phase; i.e., the surface atoms may not be coherently spin-coupled with the inner atoms.[1] The S/V of our as-prepared γ-Fe_2O_3 nanocrystals is so big that they exhibit a very weak magnetic property. Therefore, the magnetism measurement of the sample shows the magnetism of the prepared nanocrystals seems to originate from γ-Fe_2O_3.

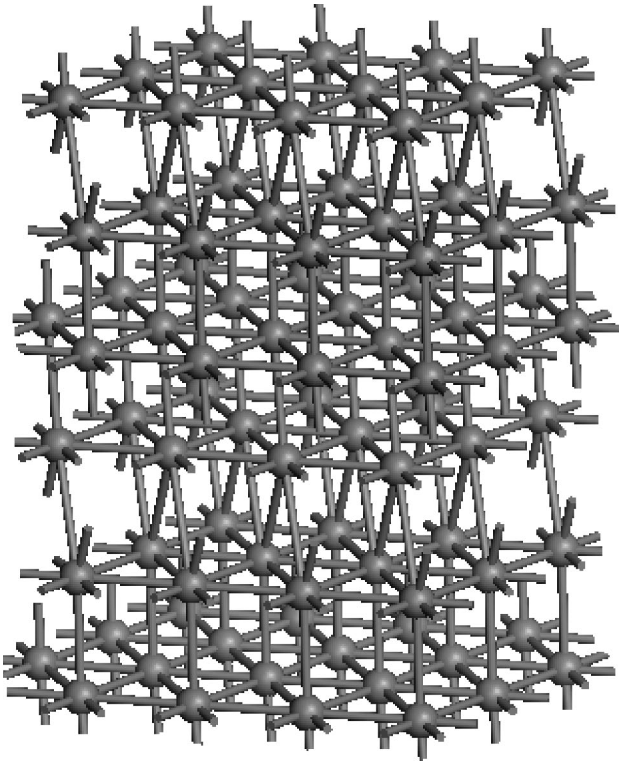

Figure 4. Schematic illustrations of DHCP structure.

On the other hand, the DHCP nanocrystals of iron in the sample are at a very low percentage. Then, they are bigger than γ-Fe_2O_3 nanocrystals. Thus, the DHCP nanocrystals of iron with small S/V would exhibit the strong magnetic property if they have magnetism. However, the SQUID result shows not only the very weak magnetism of the sample but also the weak magnetism which seems attributed to the contribution of γ-Fe_2O_3 nanocrystals. Accordingly, we deduce that that the DHCP phase of iron may be weak in magnetism or even nonferromagnetic.

Generally, in the case of iron, the cubic phase is magnetic and HCP is nonmagnetic while the magnetism of body-centered-cubic (bcc) is better than that of face-centered-cubic (fcc), as well as for the same structure; the larger the lattice parameter is, the better the magnetism will be.[24] Therefore, focusing on just iron, the better symmetry and the large lattice parameter would lead to good magnetism. As shown in Figure 4, the symmetry of DHCP phase of iron is worse than that of HCP and the lattice parameter in the $a-b$ plane

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is smaller than that of HCP.[19] Thus, these results show that the DHCP phase of iron seems nonmagnetic, which matches our experimental results above.

The DHCP phase of iron is a metastable phase (the high-pressure phase) that only exists under the condition of the pressure of 35−40 GPa.[15] Why are the DHCP nanocrystals of iron stable under room temperature and ambient pressure? On the basis of our recent considerations,[18] we suggest that the nanosized confinement effect from nanocrystals seems responsible for the stability of the DHCP phase of iron. In detail, the thermodynamic driving force from the giant interior pressure induced the nanosized curvature of nanocrystals would push the metastable phase at the nanometer scale into the stable phase.[25] In general, the stability of metastable phase at the nanometer scale, e.g., the transition pressure at the nanometer scale, is quite different from that of bulk.[26] Meanwhile, any perturbation from the environment can influence the energy of the metastable phase and make the structure out of equilibrium. As long as the perturbation continues long enough, there will be enough energy accumulated to drive the reconfiguration of lattice structure, which can trigger a phase transition from metastable to stable phase. This behavior is confirmed by the comparing XRD result in Figure 1a.

IV. Conclusion

In summary, the DHCP phase of iron, a high pressure, has been observed upon PLIIR, and meanwhile the corresponding DHCP nanocrystals are prepared. SQUID measurement exhibits that the DHCP nanocrystals of iron may be nonferromagnetic. This study indicates that the metastable phase that are unstable in bulk under normal conditions may be stable at the nanometer scale due to the nanosized confinement effect.

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