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Magnetite 3D Colloidal Crystals Formed in the Early Solar System 4.6 Billion Years Ago

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S *Supporting Information*

ABSTRACT: Three-dimensional colloidal crystals made of ferromagnetic particles, such as magnetite (Fe_3O_4), cannot be synthesized in principle because of the strong attractive magnetic interaction. However, we discovered colloidal crystals composed of polyhedral magnetite nanocrystallites of uniform size in the range of a few hundred nanometers in the Tagish Lake meteorite. Those colloidal crystals were formed 4.6 billion years ago and thus are much older than natural colloidal crystals on earth, such as opals, which formed about 100 million years ago.[1] We found that the size of each individual magnetite particle determines its morphology, which in turn plays an important role in deciding the packing structure of the colloidal crystals. We also hypothesize that each particle has a flux-closed magnetic domain structure, which reduces the interparticle magnetic force significantly.

Carbonaceous chondrites, which comprise very primitive solar system materials, are known to contain micrometer-sized polyhedral magnetites called magnetite framboids.[2,3] It was suggested that the magnetites were formed during a period of aqueous activity in the parent asteroids[4] because the magnetites occur together with phyllosilicates and carbonates in the hydrated carbonaceous chondrites. On the basis of the abundance of short-lived radionuclide ^{53}Mn in carbonate crystals in the Orgueil CI carbonaceous chondrite, it was inferred that the aqueous alteration took place very early in the history of the solar system, namely, 20 million years after the formation of the earliest solar system condensates 4.6 billion years ago.[5] The $^{18}O/^{16}O$ isotopic ratio of this meteorite indicated that the parent asteroid had a water/rock mass ratio of 1.2 and a temperature close to 0 °C[6] during aqueous alteration.

The Tagish Lake meteorite fell to earth in January 2000 and was recovered immediately.[7] This meteorite is an invaluable specimen because of its limited exposure to the terrestrial environment.[8,9] It is a hydrated carbonaceous chondrite that abounds with magnetites, which are considered to have been formed during aqueous alteration 4.6 billion years ago in a similar way as for the other chondrites of the same type. The most striking feature of this meteorite is occurrences of magnetite. This meteorite is relatively porous in comparison with the other metamorphosed meteorites, and its original texture has been preserved; it contains many pore spaces that are now filled with secondary minerals, mainly with magnetite. The polyhedral magnetite nano- and microcrystallites are generally distributed randomly throughout the entire meteorite. However, we found new three-dimensional (3D) ordered structures in the meteorite, comprising 10^3-10^4 crystalline polyhedral magnetite (Fe_3O_4) nanoparticles (Figure 1) with sizes of 110−680 nm. Such 3D ordered crystals are known as colloidal crystals. They have been the subject of considerable interest in the fields of colloidal and materials science and find applications in, among others, optics and photonic crystals.[10−12] Extraterrestrial colloidal crystals, however, have not been reported to date.

The morphologies and structures of the magnetite colloidal crystals were examined by field-emission scanning electron microscopy (FE-SEM). The inner structure of the fine particles was examined using transmission electron microscopy (TEM). The size distribution of the whole collection of magnetite particles in the meteorite (i.e., both isolated and individual constituent particles of the colloidal crystals) peaks at 200−300 nm, and more than 99% of the particles are smaller than 600 nm. Particles with diameters greater than 1 μm were occasionally found.

Figure 1a shows a colloidal crystal composed of 124 ± 6 nm octahedral magnetite particles bounded by {111} faces. The particle morphology was confirmed by FE-SEM [see Figure S1 and the text in the Supporting Information (SI)]. Figure 1b shows a colloidal crystal composed of 246 ± 3 nm rhombic-dodecahedral

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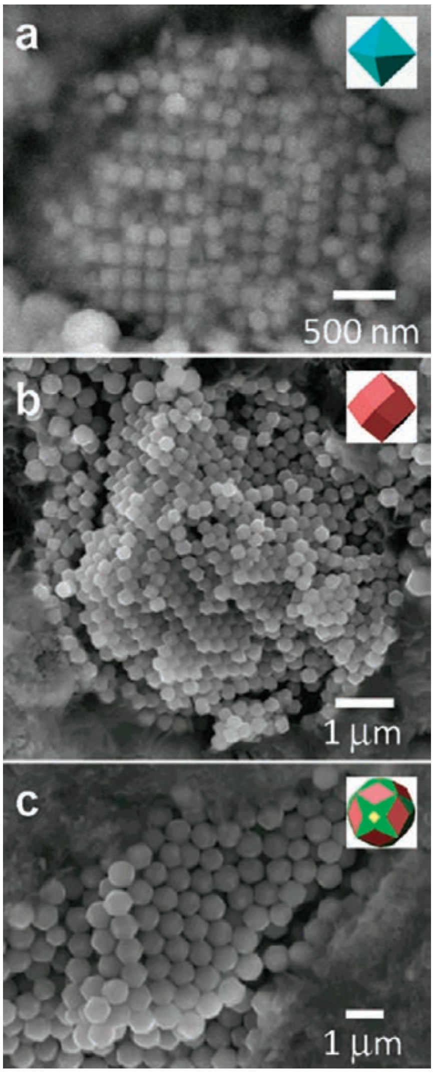
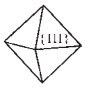
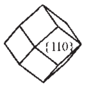
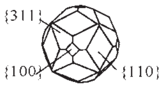


Figure 1. FE-SEM images of magnetite (Fe_3O_4) colloidal crystals in the Tagish Lake meteorite. The morphology is inset at the upper right in each image. (a) Colloidal crystal with the bct structure composed of octahedral, crystalline nanoparticles of Fe_3O_4 bounded by {111} faces. (b) Colloidal crystal with the fcc structure. The morphology of the constituent particles is rhombic-dodecahedral, bounded only by {110} faces. (c) Colloidal crystal with the fcc structure composed of particles bounded by {100}, {110}, and {311} faces.

particles bounded by {110} faces; the packing structure is face-centered cubic (fcc). Figure 1c shows a colloidal crystal composed of 657 ± 20 nm particles bounded by {100}, {110}, and {311} faces. The packing structure of the top three layers of the colloidal crystal is fcc. In the meteorite, the colloidal crystals of the type shown in Figure 1b are dominant in comparison with the other two types. From an observation of 40 colloidal crystals, the numbers of the types in Figure 1 a−c are 7, 29, and 4, respectively. Isolated colloidal crystals sometimes occur, but often a group of ∼10 colloidal crystals were found in micrometer-scale voids, which are randomly distributed in the meteorite. In the latter case, the colloidal crystals can be all of the same type or a mixture of different types. Colloidal crystals do not appear when the constituent particles have diameters greater than 700 nm. These observations suggest that the morphology of the magnetite particles is determined by their size.

Table 1. Morphologies of the Particles versus Packing Structures of the Colloidal Crystals

Diameter of constituent particles [nm]	Morphology of constituent particles	Packing structure of colloidal crystals	Lattice parameter of colloidal crystals [nm]
124 ± 6[a]		b.c.t.	a, b = 142, c = 167
246±3[a]		f.c.c.	a, b, c = 291
657±20[b]		f.c.c.	a, b, c = 926

[a] Characteristic diameter (i.e., diameter of a sphere with the same volume). [b] Diameter of the circumscribed sphere.

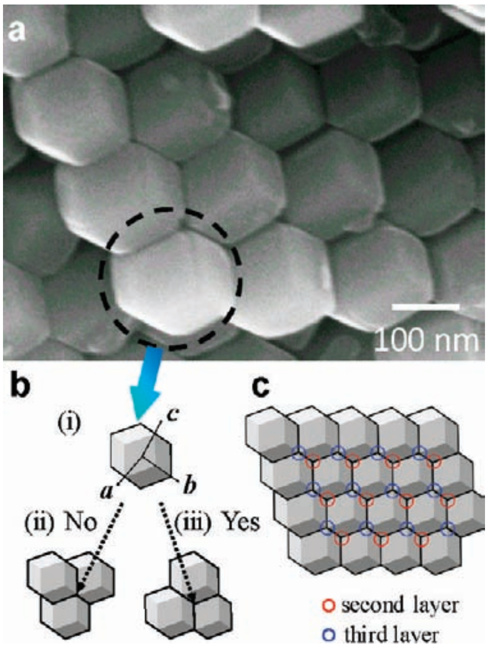


Figure 2. Packing model for pure rhombic-dodecahedral particles in a space-filling fcc lattice. (a) Enlarged FE-SEM image of a colloidal crystal of the type shown in Figure 1b. (b) Packing of the rhombic-dodecahedral particles: (i) View of a rhombic dodecahedron. (ii, iii) Two ways to fit these particles into the same plane. If one more particle is placed at the center of the other three particles, (iii) shows a perfect fit, whereas for (ii) the four particles cannot be fitted together without creating gaps. (c) Obeying the rule illustrated in (b), the stacking results in an ABCABC... (i.e., fcc) structure.

The packing structure of the colloidal crystals depends on the morphology of the constituent particles (Table 1). Possible packing structures of the colloidal crystal shown in Figure 1a are fcc or body-centered tetragonal (bct). Theoretically, the ratios of the distance between nearest neighbors and the particle width are 1.00 in the fcc {001} plane and >1.00 in the bct {001} plane, assuming contacting octahedrons between successive (001) layers. From the FE-SEM image shown in Figure 1a, the average value of this ratio is 1.11 ± 0.05, indicating that the particles do

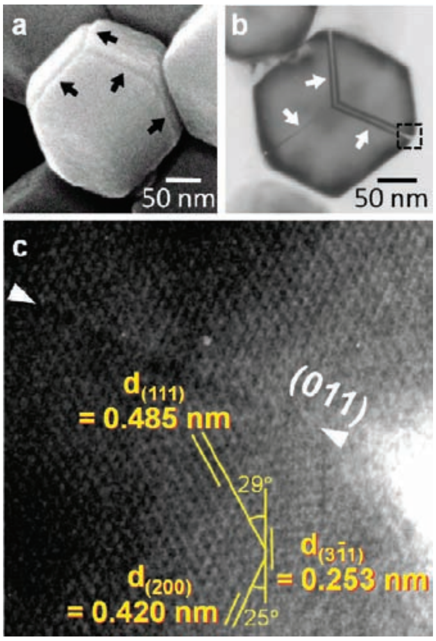


Figure 3. Dodecahedral particle of magnetite with defects at certain edges. (a) FE-SEM image of a magnetite particle with a size of 246 nm and a rhombic-dodecahedral shape. Depressed areas at certain edges are indicated by black arrows. (b) TEM image of the same type of magnetite particle viewed along ⟨111⟩. Distinct boundaries (white arrows) can be observed at the positions corresponding to the depressed areas in (a). (c) HRTEM image viewed along $[01\bar{1}]$ showing the area indicated by the dashed line in (b); {200}, {111}, and $\{\bar{3}11\}$ lattice planes are imaged, as well as the (011) fault plane, which is indicated by the two white triangles. This particle has planar fault planes at the positions indicated by the arrows in (a) and (b). The colloidal crystal of Figure 1b is composed entirely of such magnetite particles.

not contact each other within one layer parallel to {001}. This indicates bct packing in which the (slightly truncated) octahedrons are ordered with their ⟨100⟩ axes parallel to the ⟨100⟩ directions of the colloidal crystal (see the SI text and Figure S2). Figure 2 explains the relationship between the morphology of the particles and the packing structure for the colloidal crystals of the type shown in Figure 1b. Figure 2a is a magnification of Figure 1b. Each particle is a rhombic dodecahedron bounded by only {110} faces [Figure 2b(i)]. This morphology is a space-filling polyhedron. As shown in Figure 2b(ii,iii), three particles can fit together in the same plane in two ways. It is impossible for a fourth particle to fit without creating gaps in the case of Figure 2b(ii). Consequently, particles of the next layer can occupy only the positions shown in Figure 2b(iii). Such a stacking of particles results in the ABCABC... arrangement (Figure 2c), which corresponds to the fcc structure. This is different from the case of spherical particles, which have two equivalent placements of the next layer, making hexagonal close-packed (hcp), fcc, or mixed structures possible. The magnetite particles comprising colloidal crystals of the type shown in Figure 2 are all bounded by only {110} faces, which is an unexpected morphology in view of their fcc crystal structure.[13] Therefore, the detailed structure of the dodecahedral particles was examined.

Figure 3a shows a magnified FE-SEM image of one rhombic-dodecahedral particle of the aggregate shown in Figure 2a; certain edges are rounded and show the presence of slight depressions, as indicated by the black arrows. To reveal the crystal structure, these magnetite particles were observed using TEM (Figure 3b). There are clear boundaries in the particles (white arrows), and these correspond to the depressed areas observed by FE-SEM (Figure 3a). Figure 3c is a high-resolution TEM (HRTEM) image of the area highlighted by the dashed square in Figure 3b. It can readily be recognized that the depressed area in Figure 3b is related to a defect plane parallel to {011}, suggesting that this particle has a number of twin planes, in a similar way as encountered for multiply twinned metal particles.[14] However, twinning along {110} has not been previously reported for magnetite; the commonly observed twinning is spinel-type, which is a mirror-type twinning along {111}.[15] From the HRTEM image and the cubic symmetry of the crystal, it follows that the crystallographic orientation of the two parts adjacent to the {110} fault plane are either identical, related by a mirror plane parallel to this plane, or related by a twofold axis perpendicular to it. As in the magnetite point group $m\bar{3}m$, the {110} plane is a mirror plane with a twofold axis perpendicular to it, and application of the two operators leads to identical orientations of the two parts. This implies that the defect planes are stacking faults or antiphase boundaries[16,17] rather than twins. The presence of the planar faults in the dodecahedral particles points to a growth history somewhat different from that of the defect-free magnetite particles of other sizes. This difference might also lead to the observed dodecahedral morphology.

To form a colloidal crystal, an appropriate repulsive force between the particles in the solvent is necessary.[18,19] However, single-domain magnetite particles have a strong attractive interaction due to magnetic forces and do not disperse in solution, as follows from Derjaguin−Landau−Verwey−Overbeek (DLVO) calculations[20,21] (see the SI text and Figure S5). This prevents colloidal crystallization and leads only to disordered aggregates or chain structures in solution.[22] To overcome this difficulty of colloidal crystallization, we have to consider how to reduce the magnetic interaction. There are two possibilities: (i) each magnetite particle is smaller than the critical size for superparamagnetism and (ii) each has a flux-closed magnetic structure. In the former case, if the size of a magnetite particle is less than ∼10 nm, it loses its magnetic force. As the size of the magnetite particles in the meteorite exceeds this critical size for superparamagnetism, they exert magnetic forces.

In the latter case, a flux-closed magnetic structure is known to reduce the magnetic interaction to a large extent. A submicrometer-sized magnetic particle larger than 100 nm typically has a multiple magnetic domain structure. This often leads to a flux-closed structure,[23,24] such as the vortex structure,[25] in which the magnetic forces are reduced considerably, a prerequisite for the formation of colloidal crystals.

Measurements on the colloidal crystals by magnetic force microscopy (MFM) showed the existence of attractive and repulsive magnetic interactions between the MFM tip and the particles in the crystal. Spin-polarized SEM of an isolated particle revealed an unusual core−shell structure composed of two different magnetic domains (see part 2 in the SI). This may relate to the substantial reduction of the magnetic interaction forces.

The formation of colloidal crystals implies several restrictions on the growth conditions in the meteorite. First, a certain amount of solution water must have been present in the meteorite to disperse the colloidal particles. The solution water must have been confined in small voids, in which colloidal crystallization takes place.[18] Since for a given colloidal crystal the particles have identical size and morphology, it follows that their nucleation must have taken place at the same moment in a short period of time, with no further nucleation occurring during subsequent growth. This points to a sudden change of the conditions in the meteorite, for instance, a change in temperature or pressure, which rapidly altered the supersaturation of the solution.

Reproducing the formation of magnetite colloidal crystals in laboratory experiments provides important information on the hydrous conditions in the meteorite parent body. As discussed above, magnetic interactions hinder colloidal crystallization. Conversion of nonmagnetic particles to magnetic ones is an alternative route to circumvent this problem. In that case, after formation of colloidal crystals by nonmagnetic particles, they were converted into magnetite. One of the candidates as a precursor of magnetite is iron sulfides, which coexist in the meteorite and in some cases do not have magnetic interactions.

We believe that, if synthesized, magnetite colloidal crystals have promising potential as a novel functional material. Different polyhedral shapes of the constituent particles can result in different structures or packing densities of the colloidal crystals, which again would change their photonic band gap properties.[26] Moreover, applying a magnetic field in combination with a suitable surfactant allows for tunable production of colloidal crystals in which the lattice properties can be changed.[27] We think that magnetite particles can create more complex structured colloidal crystals with improved control.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Body-centered stacking of {001} truncated octahedra, magnetic observations using MFM and spin-polarized SEM, DLVO curve of interacting magnetite particles, and complete ref 7. This material is available free of charge via the Internet at http://pubs.acs.org.

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