Supporting information

Microscopic states and the Verwey transition of magnetite nanocrystals investigated by nuclear magnetic resonance

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NMR Spectra of the 16 nm, 40 nm, 80 nm, and bulk (7 μm) samples

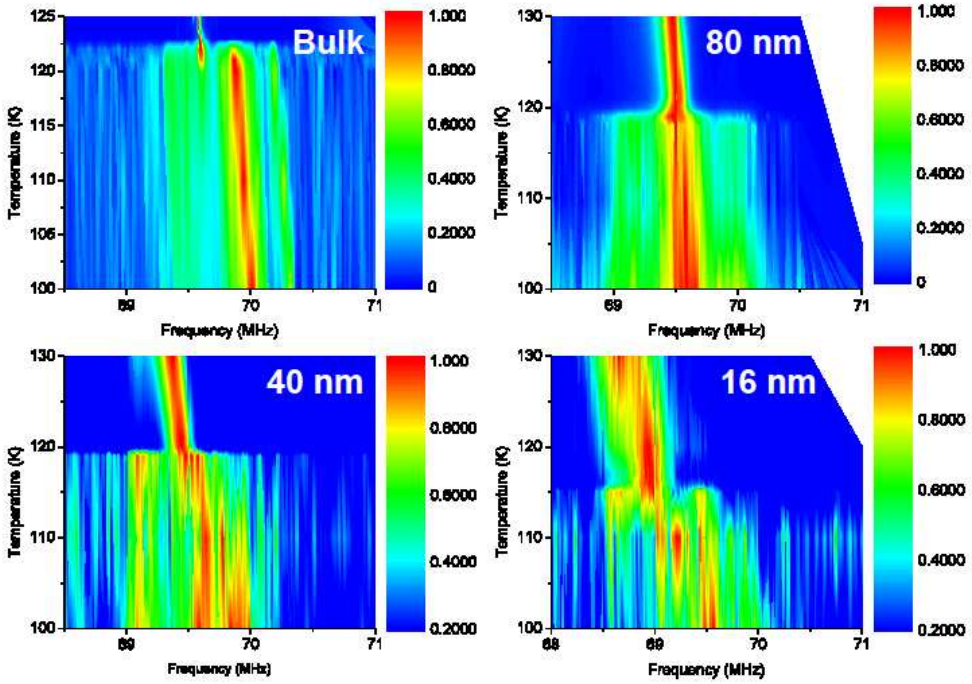

Figure S1 – ^{57}Fe NMR spectral intensity of the 16 nm, 40 nm, 80 nm, and bulk (7 μm) sample obtained at temperature around T_V .

^{57}Fe NMR spectra of the magnetite nanocrystals (16, 40, 80 nm) and bulk sample obtained at various temperatures between 100 K and 130 K are shown in Figure S1. All these samples share the features of the 25 nm sample (Figure 2a). The spectral linewidth remains constant, except in the range of temperatures near the T_V. The transition temperature of the samples are 123 K (bulk), 120 K (80 nm), 119 K (40 nm), and 115 K (16 nm), respectively.

Methods

The 7 μm sample was prepared by thermal annealing at 1300 □ for 24 hours in pure CO gas atmosphere to obtain exact stoichiometry. The temperature of tube furnace was increased with heating rate of 180 □ / hrs. After annealing, it had been stored in a glove box to prevent oxidation.

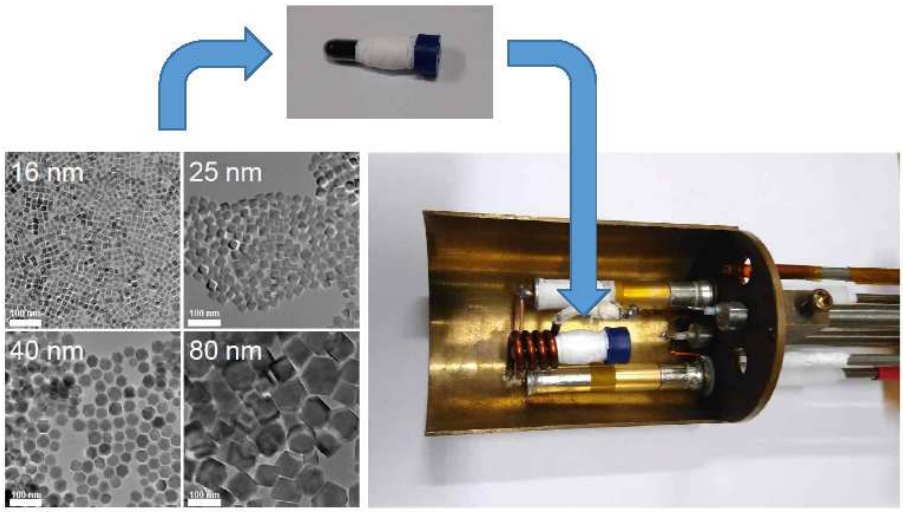

Figure S2 – NMR probe head setup

Each of magnetite NCs was sealed in a 5-mm NMR tube inside the argon-filled glove box. The tank circuit consists of an RF coil and two variable capacitors. Sample tube was placed inside the RF coil. Resonance frequency of the circuit was controlled by two variable capacitors (NMTM120CFSK of Voltronics). In the frequency range of 67~71 MHz, typical Q-factor is 50~100. Pulsed NMR was performed by the home-built spectrometer, which consists of an RF generator (Fluke, 6060B), a pulse generator (SpinCore, PB12-50), modulators (Mini-Circuits, ZYSWA-2-50DR; ZFSCJ2-1; ZAS-1), homodyne type demodulators (Mini-Circuits, ZSCQ-2; ZFSC-2-1W; ZP-1), an amplifier (Amplifier Research, 1000LP), a preamplifier (MITEQ, AU-1467), and an oscilloscope (GaGe, CompuScope 12100).

We measured Spin-Echos at every 0.5 MHz and summed up their Fast-Fourier-Transformed spectra to get a complete spectrum. Spectra were obtained at every 10 K, and additionally, every 1 K for the temperature around the T_V. The spin-spin relaxation time was determined by varying the interval between two pulses of the Hahn echo sequence.

Because of difference in enhancement factors in domain and domain walls, the RF pulse power required to the NMR signal from the domain wall is small, compared to the signal from the domain. We can distinguish the signal of the domain from that of the domain wall since the latter disappears in magnetic field. We controlled the RF pulse power (from mV to ~100 V peak-to-peak) to obtain the signals only from the domain.

Transmission electron microscopy (TEM) images were obtained using a JEOL EM-2010 microscope. The sample grid was prepared by dispersing the nanocrystal in toluene and by dropping the solution onto a copper grid coated with carbon film.