BL-8B/2023G027, 2025G018

Strong Correlation between Crystal Structure and Electronic State in Mn_3O_4 nanoparticles

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1 Introduction

Nanoparticles possess interesting magnetic properties and crystallographic structures, which differ from those of bulk crystals, because of high proportion of surface area and finite size effects. It is expected that difference of magnetic properties and crystal structure between nanoparticles and bulk crystal becomes prominent owing to the enhancement of modulation of energy state at surface of nanoparticle as particle size decreases. In terms of crystallographic structure, the existence of edges and defects at surface of nanoparticles induces changes in translation symmetry with decreasing particle size. As particle size decreases, the modulation of electronic state and structural symmetry at surface of nanoparticles affects the overall magnetic properties and crystal structure of nanoparticles. In the case of antiferromagnetic nanoparticles with magnetic moments at the surface of a particle, the lattice strain and distortion of crystallographic structure significantly affect the magnetic properties. For instance, the magnetic properties of the NiO nanoparticles with particle size of 2–22 nm were strongly correlated with the rhombohedral distortion of the rock-salt structure and lattice strain [1]. It is expected that a competition between thermal shrinkage and lattice strain in the nanoparticles brings out characteristic changes in electronic state, magnetic property and crystal structure. The combination of electron spin resonance (ESR) and X-ray structural analysis is an effective technique to investigate the intrinsic magneto-structural correlations in nanoparticles.

The magnetic properties of spinel oxide Mn_3O_4 nanoparticles are strongly influenced by particle size, with the size-dependent effect varying according to both the particle size regime and synthesis method employed [2-6]. Mn_3O_4 nanoparticles are expected to demonstrate characteristic temperature-dependent variations in both crystal structure and magnetic properties. In addition, the temperature dependences of the crystal structure and electron spin resonance (ESR) spectrum are also influenced by particle size owing to the competition between magnetic interactions, thermal contraction, and lattice strain within the Mn_3O_4 nanoparticles. In this study, we investigated the temperature dependence of the crystallographic structure and electronic state of Mn_3O_4 nanoparticles through X-ray diffraction (XRD) and ESR measurements down to 100 K, aiming to deepen the understanding of the correlation between crystal structure and electronic state and magnetic phase diagram as function of particle size.

2 Experiment

Mn_3O_4 nanoparticles with particle sizes of d = 7−20 nm were synthesized in the pores of mesoporous silica SBA-15 [6]. Powder XRD measurements were carried out down to 100 K using the a Debye-Scherrer camera at BL-8B. The incident X-ray energy was set to 18 keV, and the wavelength was calibrated using the XRD patterns of CeO_2 powder. ESR measurements were performed between 100 K and 320 K using an X-band spectrometer (JOEL JES-RE2X) equipped with a cryostat.

3 Results and Discussion

The XRD patterns for all Mn_3O_4 nanoparticles with d = 7−20 nm suggested that no phase transition in the crystal structure occurred between 100 K and 285 K. The lattice constants a and c, tetragonal distortion $c/\sqrt{2}a$, and unit cell volume V, of the Mn_3O_4 nanoparticles exhibited characteristic temperature dependences. Figure 1 shows temperature dependence of lattice constants for d = 9.1 nm. The values on the vertical axis were normalized using the lattice constant at 285 K. The lattice constant a displayed two local minima at approximately 170 K and 240 K, as indicated by the red arrows in Fig. 1. Similarly, the lattice constant c and unit cell volume V for all nanoparticles displayed two local minima, as denoted by the blue and brown arrows in Fig. 1, respectively. Tetragonal distortion, which characterized the Jahn−Teller distortion in Mn_3O_4, also displayed two local minima in its temperature dependence, as indicated by green arrows in Fig. 1. The temperature dependence of the tetragonal distortion closely mirrored that of the lattice constant c. These results indicate that the Mn_3O_4 nanoparticles exhibited anisotropic modulation of unit cell and spontaneous magnetostriction.

The ESR absorption spectrum for the Mn_3O_4 nanoparticles contained a broad component and six narrow spectra corresponding to the hyperfine splitting arising from the interaction between the electronic spins S = 5/2 and nuclear spin I = 5/2 of the Mn^{2+} ions [6, 7]. The hyperfine-split absorption lines were attributed to Mn^{2+} ions located on the nanoparticle surface [6]. The ESR spectra of the nanoparticles were reproduced by the sum of two components: a single line (SL) and hyperfine structure (HS) above 300 K. As temperature decreased, additional hyperfine splitting absorption lines emerged at two distinct temperatures, depending on particle size. All observed ESR spectra for the synthesized Mn_3O_4 nanoparticles could be reproduced by a combination of a SL and some HS components. The temperature dependence of the (a) g factor, (b) integrated intensity, (c) linewidth ΔH, and (d) hyperfine coupling constant for the divided SL and three HS components of nanoparticles with $d = 9.6$ nm, is shown in Fig. 2. As the temperature decreased, the g factor of the SL component displayed two peaks at approximately 240 and 180 K. The HS1 component displayed a minimum at approximately 215 K and remained nearly constant below 180 K. For HS2 component, the g factor displayed a minimum at 240 K and remained almost constant below 220 K. In constant, the HS3 component exhibited a hump at approximately 200 K and remained almost constant below 170 K. The integrated intensity of absorption line for SL component exhibited a hum at 230 K and increased monotonically as the temperature decreased. The HS1 component displayed two peaks at approximately 270 and 190 K, whereas the HS2 component exhibited two small peaks at approximately 230 and 180 K. Conversely, the HS3 component gradually decreased and remained constat below 190 K. The ΔH of the SL component gradually decreased with two local maxima observed at approximately 260 K and 190 K. For the HS1 component, ΔH displayed two peaks at approximately 260 and 200 K and remained constant below 170 K. The HS2 component decreased monotonically and remained constant below 170 K as the temperature decreased. The HS3 component decreased monotonically and then stabilized below 190 K. As the temperature decreased, hyperfine coupling constant of the HS1 component displayed a hump at approximately 250 K, decreased at 250 K and exhibited second hump at 170 K and then increased below 150 K. The HS2 component exhibited two peaks at approximately 230 and 170 K. In contrast, the HS3 component displayed a maximum at approximately 200 K and remained constant below 170 K.

The obtained ESR parameters, such as the g factor, ΔH, integrated intensity, and hyperfine coupling constant, also displayed inflection points and/or local extrema at the same temperatures where the lattice constants displayed local minima. These temperature dependences were consistently observed for all investigated particle size. The observed correlations between the crystal structure and ESR spectrum parameters in the Mn_3O_4 nanoparticles indicates that the modulation of the Jahn-Teller distortion caused by the variations in bond lengths and angles around Mn ions, driven by variations in lattice constants, modulate the crystal field environment. It is suggested that a characteristic spontaneous magnetostriction occurred in the Mn_3O_4 nanoparticles. The changes in the electronic state at the surface of nanoparticles increased with decreasing particle size, owing to an increase in the ratio of surface area to particle volume, resulting in an increased change in lattice constants with temperature as particle size decreased. It is concluded that the changes in the ESR absorption spectrum were attributed to changes in electronic state due to the distortion of crystallographic structure, that is, appearance of characteristic spontaneous magnetostriction effect within Mn_3O_4 nanoparticles.

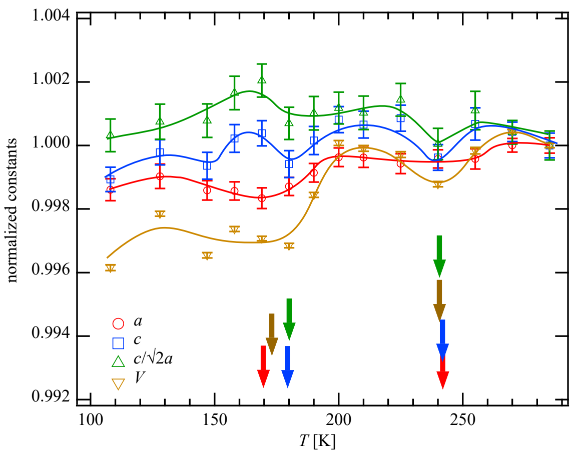

Fig. 1: Temperature dependence of the lattice constants normalized to their respective values at T = 285 K for Mn_3O_4 nanoparticles with $d = 9.1$ nm. The arrows indicate the temperatures at which the lattice constants exhibited local minima.

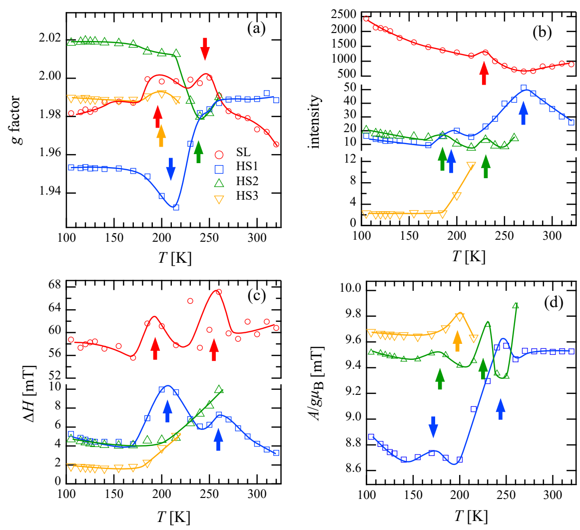

Fig. 2: Temperature dependence of (a) g factor, (b) integrated intensity, (c) linewidth, and (d) hyperfine coupling constant for Mn_3O_4 nanoparticles with $d = 9.6$ nm. Arrows indicate the temperatures at which the ESR parameters exhibited local maxima and/or minima.

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