Formation and magnetic properties of nanoclusters with the doubled lattice constant structure of α-LiFeO$_2$

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Powders of α-LiFeO$_2$ exhibited the x-ray diffraction pattern of cubic unit cell structure (a = 4.157 Å). Wavy shaped diffuse scattering due to short-range ordering of Li$^+$ and Fe^{3+} ions was observed in both electron diffraction patterns of the cubic structure (a = 4.2 Å) and of doubled unit cell structure (a = 8.3 Å). The size of grains surrounded with (111) planes of the doubled unit cell structure was about 40 Å, and the interfaces were phase boundaries. Splitting between field-cooled and zero-field-cooled dc susceptibilities was observed at ≈90 K. Below ≈90 K, the field-cooled susceptibility increased monotonically and the zero-field-cooled susceptibility deviated below the field-cooled one with lowering temperature. A broad shoulder in the zero-field-cooled susceptibility centered at ≈40 K. The real part of ac susceptibility exhibited a cusp at ≈90 K with a broad shoulder centered at ≈60 K. The third harmonic nonlinear susceptibility showed no sharp peak below 200 K. Observed magnetic behavior of α-LiFeO$_2$ can be understood as formation and progressive freezing of the ferromagnetic nanoclusters.

The unit cell of α-LiFeO$_2$ has NaCl-type structure, in which both Li$^+$ and Fe^{3+} ions occupy randomly octahedral sites in a cubic closest packing of O^{2-} ions [1,2]. A magnetic transition around 90 K and a ferromagnetic spin coupling in a (111) plane resulting in a net antiferromagnetic interaction between alternate (111) planes were reported by Cox et al. [3]. Anderson et al. [4] reported only an antiferromagnetic ordering at 40 K. Tabuchi et al. [5] reported two anomalies at 90 K and around 40 K in zero-field-cooled dc susceptibility. It is of great interest to examine history dependence of dc susceptibility and frequency dependence of ac susceptibility in relation to microstructure for elucidation of the anomalous magnetic behavior of α-LiFeO$_2$.

We obtained single phase α-LiFeO$_2$ powders by calcination at 900 ^{o}C for 1 h in air of a mixture of Li$_2$CO$_3$ (99.95 % purity by Kanto Chemical, Japan) and α-Fe$_2$O$_3$ (99.5% purity by Wako Pure Chemical, Japan) with the molar ratio of Li : Fe = 1.2 : 1. As shown in fig. 1, we could not find any other peaks from α-LiFeO$_2$ crystal lattice. The lattice constant a of the sample was 4.15$_7$ Å, which is in good agreement with that reported earlier [2]. The Fe^{3+} state was confirmed by the Fe $2p$ electron spectrum [6]. The Fe $2p_{3/2}$ electron binding energy of the sample was 711.1 eV and the charge transfer satellite structure positioned around 716 eV, which agreed well with that

reported for Fe_2O_3 [7].

For microstructure examination at room temperature, we employed a JEM-3100FEF transmission electron microscope (TEM) having an in-column type energy filter. The filter removing inelastic scattering contribution from electron diffraction pattern is useful to observe diffuse scattering clearly [8]. For almost fractions of the sample, we observed TEM image with a fringe of spacing ≈ 4 Å and electron diffraction pattern with wavy diffuse scattering between sharp spots of the cubic NaCl-type unit cell ($a = 4.2$ Å), as shown by fig. 2a and fig. 2b, respectively.

The diffuse scattering has already been reported [9] and is interpreted as short-range ordering [10]. Though Li^+ and Fe^{3+} ions occupy the octahedral sites in NaCl structure randomly, the occupancy probability of corners is affected by the nearest neighbor cites. Eight corners of a given octahedron in the α-$LiFeO_2$ crystal are always occupied by four Li^+ ions and four Fe^{3+} ions, but the ordered arrangement shown in fig. 2c is possible. The stoichiometry in each octahedron is always kept locally. This short-range ordering structure causes the diffuse scattering on a surface described by a following equation in reciprocal space [11].

$$\cos \pi h + \cos \pi k + \cos \pi l = 0,$$

where h, k and l are Miller indices. The wavy shape of the diffuse scattering is a cross section of the surface.

In some fractions of the sample, we found mosaic structure with the fringe of doubled spacing in TEM images, as shown in fig. 3a. The electron diffraction patterns accompanied with the wavy diffuse scattering on the spots of cubic structure with a doubled lattice constant $a = 8.3$ Å, as shown in fig. 3b. The grain size of the mosaic structure was about 40 Å, and it was uniform. The grains were surrounded with (111) planes, and the interfaces were phase boundaries. Since the small grains are connected with phase shift, the occupancy probability modulation is smeared out macroscopically.

It is known that a lattice constant of antiferromagnetic spin ordering structure at low temperature is twice [3]. The magnetic moments within a given (111) plane are parallel, and their direction in successive planes alternates in a positive and negative sense. This magnetic ordering can be detected by neutron diffraction, but cannot by neither x-ray nor electron diffraction. Even at room temperature, the fraction with a doubled lattice constant has chemical ordering of Li^+ and Fe^{3+} ions occupancy, and the occupancy probability is likely modulated in a (111) plane, and the modulation phase in successive planes alternates.

Such a ordering of Fe^{3+} ions at room temperature with (111) planes of the doubled unit cell structure should form nanosized ferromagnetic clusters with lowering the temperature in α-$LiFeO_2$ since the Fe^{3+} spins ferromagnetically ordered in the (111) plane are uncompensated at surfaces of the grains sizing about 40 Å. Therefore, we examined magnetic properties of the α-$LiFeO_2$ sample using a Quantum Design MPMS 5S superconducting quantum interference device magnetometer. A cooling history (zero-field-cooled and field-cooled) dependence of the dc magnetization (M) was measured in the field (H) of 100 and 300 G. After cooling the sample in zero-field from room temperature to 5 K, M_{ZFC} data were collected applying the field while warming to 200 K, and then M_{FC} data were collected in the field while cooling the sample from 200 K to 5 K.

The history dependent dc susceptibilities ($\chi = M/H$), χ_{ZFC} and χ_{FC}, of the sample are displayed in fig. 4. Two anomalies at ≈ 90 K (kink in both χ_{ZFC} and χ_{FC}) and ≈ 40 K (broad shoulder in χ_{ZFC}) were observed. These critical temperatures are in agreement with the previous results [3-5]. Above the bifurcation point (the temperature at which χ_{ZFC} and χ_{FC} curves merge) of ≈ 90 K, both χ_{ZFC} and χ_{FC} decreased rapidly with increasing the

temperature. Below the bifurcation point, χ_{ZFC} deviated from χ_{FC}, and χ_{FC} rose continuously with lowering the temperature. The sharp rise of χ towards the bifurcation point with a decrease of temperature mirrored a growth of ferromagnetic ordering of Fe^{3+} spins within a (111) plane in both the cubic unit cell ($a = 4.2$ Å) and the structure with doubled lattice constant ($a = 8.3$ Å). Falling of χ_{ZFC} below the bifurcation point reflected antiferromagnetic ordering between the ferromagnetic (111) planes. Thus, growth of intraplane ferromagnetic ordering simultaneously resulted in formation of interplane antiferromagnetic ordering. However, the ferromagnetically ordered Fe^{3+} spins within the (111) planes are uncompensated at surfaces of the grains with the structure of doubled lattice constant ($a = 8.3$ Å). Therefore, the chemical clusters sizing about 40 Å resulted in ferromagnetic nanoclusters, and then they randomly froze as temperature is further decreased. Therefore, the shoulder in χ_{ZFC} ($\approx$40 K) matches to the freezing temperature (T_f) of ferromagnetic α-LiFeO$_2$ nanoclusters. The large difference between χ_{ZFC} and χ_{FC} below T_f indicates absence of true long-range ordering, and presence of short-range ferromagnetic ordering within the cluster. In usual spin glasses, χ_{FC} is almost flat below the bifurcation point [12]. Monotonically increased χ_{FC} below the bifurcation point is similar to that reported for cluster glass materials [13-15] rather than for usual spin glasses.

Progressive freezing of ferromagnetic α-LiFeO$_2$ nanoclusters began immediately below the bifurcation point. Freezing appears through the probability of each cluster to overcome the energy barrier E induced by the local anisotropy, and expressed in terms of relaxation time $\tau = \tau_0 \exp(E/k_B T)$, where $\tau = 1/f$ is the measuring time and τ_0 is the characteristic relaxation time. On lowering the temperature, the relaxation time increases and an anomaly in the ac susceptibility will appear at T_f when τ

becomes larger than τ_0. If the relaxation time spectrum is very broad, this anomaly in the ac susceptibility can be associated with the maximum of the distribution. Figure 5a shows the temperature dependence of the real part of ac susceptibility (χ') of the zero-field cooled sample measured at the frequency (f) from 10 to 1000 Hz with the driving field (h) of 3.5 G. The cusp positioned at $\approx$90 K, and rather broad shoulder was observed at $\approx$60 K in the temperature range where χ_{ZFC} deviates below χ_{FC}. The cusp of χ' at $\approx$90 K indicates antiferromagnetic ordering with the appearance of ferromagnetic nanoclusters. The broad distribution at a temperature immediately below the χ' cusp can be associated with the freezing of clusters in our time scale of observation. The χ' cusp was invariant from $f = 10$ to 1000 Hz, and it was the same as the bifurcation point between χ_{FC} and χ_{ZFC}. Since the shoulder in χ' curve was so broad, it was difficult to determine changes of the temperature ($\approx$60 K) from $f = 10$ to 1000 Hz, though it is higher than that of the shoulder in χ_{ZFC} ($\approx$40 K). A shift of the χ' peak to the higher temperature side with increasing the frequency can be understood as an indication of slow relaxation processes in superparamagnetic materials or spin glass materials [16]. It is well known that the relative shift of the χ' peak temperature per decade of frequency for superparamagnets is much larger than that for spin glasses [12,16,17].

It is well known that a spin glass can be specified by a divergence of the nonlinear susceptibility χ_3. The magnetization m is expressed as $m = \chi_1 h + \chi_3 h^3 + \chi_5 h^5 + \dots$, when the applied ac field $h = h_0 \sin(\omega t)$ is so small. Here, χ_1 is the linear susceptibility, and χ_3 and χ_5 are the nonlinear susceptibilities. The 3ω component can be given by

$$M_{3\omega} = -(1/4)\chi_3 h_0^3 - (5/16)\chi_5 h_0^5 - (21/64)\chi_7 h_0^7 + \dots.$$

Therefore, the real part of nonlinear

susceptibility χ'_3 is given as $\chi'_3 = (-4)\lim(M'_{3\omega}/h_0^3)$, and is proportional to higher harmonic signals of frequency 3ω. As shown in fig. 5b, the temperature dependence of χ_3 at $f = 100$ Hz with $h_0 = 3.5$ G showed no divergent peaks below 200 K. The nonlinear susceptibility measurement confirmed that the assembly is noninteracting ferromagnetic nanoclusters.

The complicated magnetic behavior of α-LiFeO$_2$ can be elucidated by formation of ferromagnetic clusters due to uncompensated spins at the surfaces of nanograins with the doubled lattice constant cubic structure. The assembly of noninteracting ferromagnetic clusters demonstrated the progressive freezing. The ferromagnetic clusters in α-LiFeO$_2$ are resulted from the local arrangement of Fe^{3+} ions of chemical clusters with the doubled lattice constant cubic structure.

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[6] The Fe $2p$ spectrum of the sample was measured by a Surface Science Laboratories SSX-100 spectrometer with monochromatized Al $K\alpha$ source in vacuum pressure less than 6 x 10^{-11} Torr at room temperature. The spectrometer was calibrated using the Au $4f_{7/2}$ (83.79 eV) electrons. Charging was referenced to the C $1s$ electrons as 285.0 eV. The estimated electron energy uncertainty was $\pm0.1_5$ eV in this experiment.

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[17] The E/k_B value, estimated from the parameters $\tau_0 = 10^{-12}$ s, $f = 1000$ Hz and $T = 60$ K, is ≈ 1200 K (≈ 100 meV).
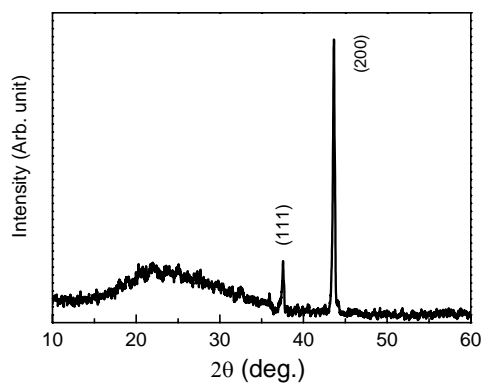
Figure 1   X-ray diffraction pattern measured with Cu *K*α radiation.

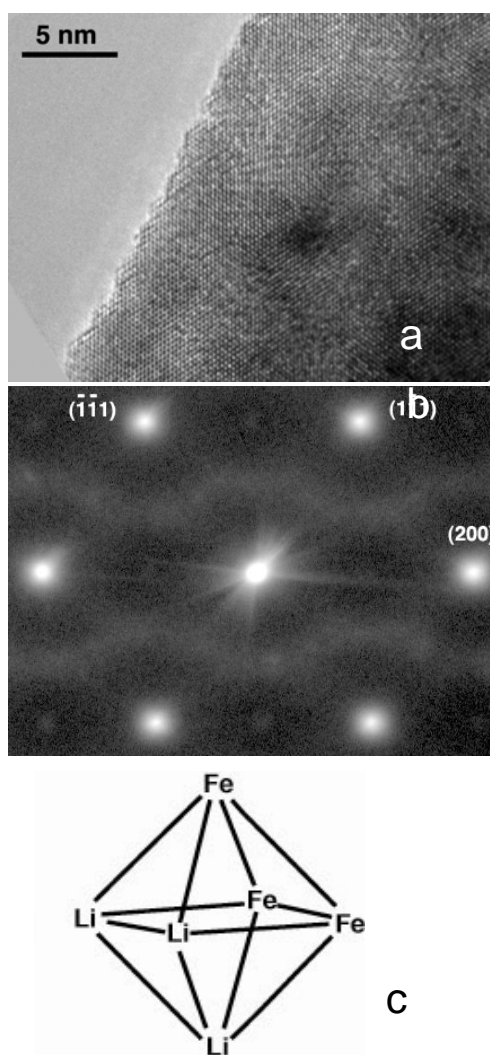
Figure 2 (a)   Transmission electron micrograph of the fraction with cubic structure
($a = 4.2$ Å).
(b)   Electron diffraction pattern from the fraction with cubic structure.
Incident direction of the electrons is [110] for all diffractions.
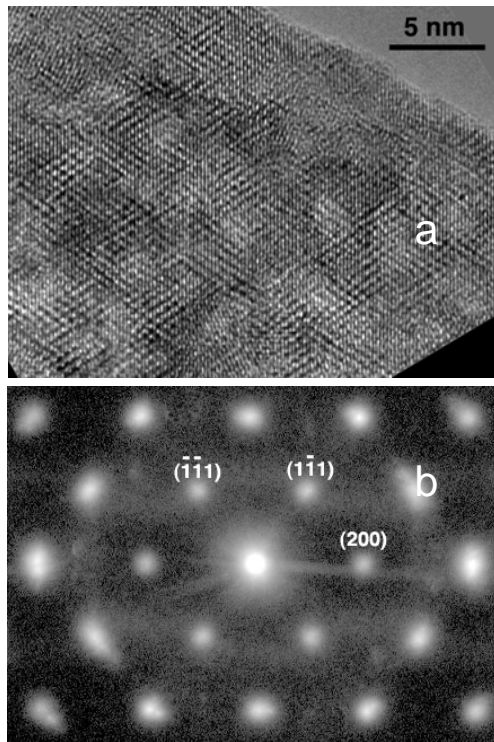(c)   Models for octahedral corner occupation.

Figure 3 (a)   Transmission electron micrograph of the fraction showing mosaic structure.
     (b)   Electron diffraction pattern from the fraction showing doubled unit cell
            structure. Incident direction of the electrons is [110] for all diffractions.
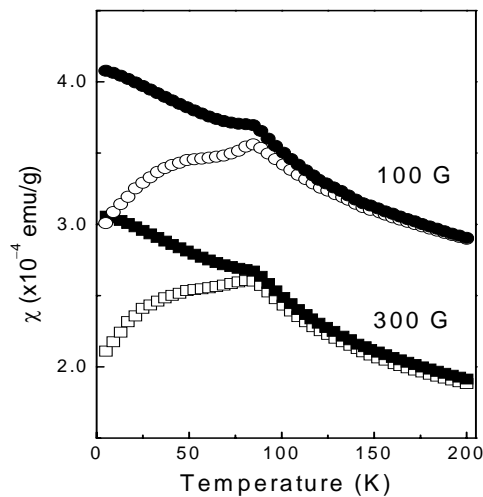

Figure 4   Temperature dependence of the zero-field cooled (open symbol) and field
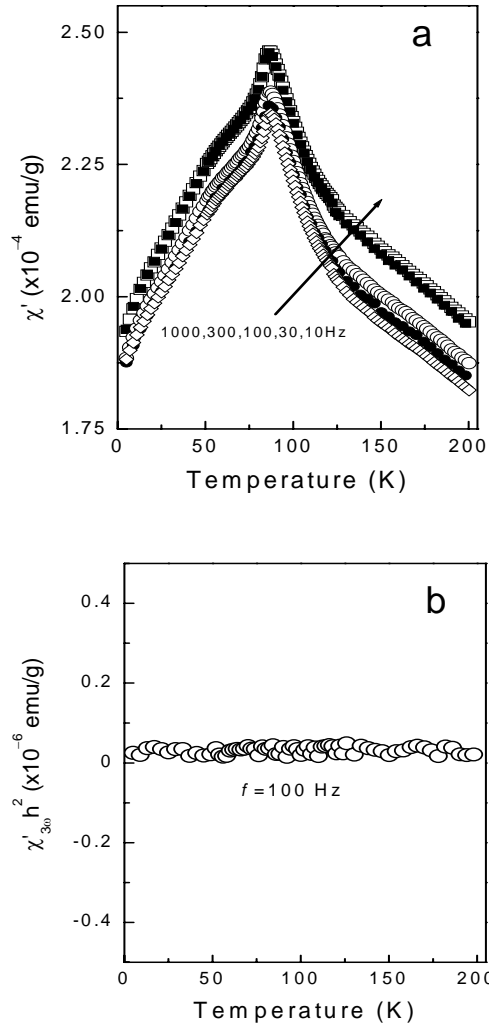   cooled (closed symbol) susceptibilities measured at $H = 100$ and 300 G.

Figure 5 (a) Temperature dependence of the real part of *ac* susceptibility measured at
$f = 10$ to 1000 Hz.

(b) Temperature dependence of the real part of nonlinear susceptibility χ_3
measured at $f = 100$ Hz.