In Situ TEM Observation of Thermally-Induced First-Order Magnetic Transition in Itinerant-Electron Metamagnetic La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> Compounds

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Defocus mode of Lorentz microscopy has revealed change in the magnetic microstructure with a first-order magnetic phase transition in La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds (0.86 ≤ x ≤ 0.90). Upon heating specimens from the ferromagnetic phase to the paramagnetic phase, magnetic domains disappear instantaneously at the Curie temperature, concurrent with a substantial change in the volume. The observations are consistent with the feature of the first-order phase transition, which gives rise to extraordinary phenomena of these compounds such as large magnetocaloric effects.

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1. Introduction

La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds with the NaZn<sub>13</sub>-type structure in a composition range 0.86 ≤ x ≤ 0.90 exhibit an itinerant-electron metamagnetic (IEM) transition. This phase transition is a first-order magnetic transition induced by applying magnetic field at a temperature slightly higher than the Curie temperature T<sub>C</sub>. A transition from the paramagnetic (P) state to ferromagnetic (F) state (or its reverse transition) can be achieved by change in temperature as well. This thermally-induced magnetic phase transition is also of the first-order in contrast with various magnetic materials undergoing the second-order transition. Note that La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds have captured much attention of researchers because of their application to magnetic refrigerations.

From a viewpoint of domain analysis by transmission electron microscopy (TEM), there are intriguing points with the magnetic phase transition in La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds. For example, the magnetic transition in La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds is accompanied by a substantial change in volume, e.g., the volume change in La(Fe<sub>0.85</sub>Si<sub>0.15</sub>)<sub>13</sub> reaches 1.5% though the space group remains unchanged. It is also interesting to compare the observation with that of martensitic transformations, which give rise to drastic changes in the space group and the crystallographic microstructure, e.g., formation of twins.

However, to the authors’ knowledge, the first-order magnetic phase transition without the change in the crystal structure such as La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds has not been observed yet by TEM. The purpose of the present work is to observe the thermally-induced first-order magnetic phase transition in La(Fe<sub>x</sub>Si<sub>1-x</sub>)<sub>13</sub> compounds (x = 0.895 and 0.90) by TEM.

2. Experiments

La(Fe<sub>0.856</sub>Si<sub>0.145</sub>)<sub>13</sub> and La(Fe<sub>0.996</sub>Si<sub>0.014</sub>)<sub>13</sub> compounds were made by arc-melting under an Ar gas atmosphere and annealed at 1323 K for 10 days. The single phase with the NaZn<sub>13</sub>-type structure was confirmed by X-ray powder diffraction. The thermomagnetization curve was measured with a SQUID magnetometer in a magnetic field of 0.2 T. Thin-foiled specimens for TEM were prepared by using a focused ion beam (FIB) system JEM-9310FIB. Figures 1(a) and 2(a) show the shape of the thin-foiled specimens. Change in the magnetic domain structure with the phase transition was observed by a defocus mode of Lorentz microscopy, by which magnetic domain walls are clearly imaged as bright and dark lines, using a transmission electron microscope JEM-3000F and a cooling stage. When observing the magnetic domains, the magnetic field at the specimen location was kept 1.5 T higher than the Curie temperature.
position was reduced to 0.2 mT. The magnetization distribution was examined by solving the transport of intensity equation\(^7,8\) on Lorentz micrographs using a commercial code QPe. The equation relates the image contrast of Lorentz micrographs with the phase of electron waves traversed a magnetic thin film. The equation can be expressed as
\[
\nabla_\perp \cdot \left[I(r_\perp, \Delta f)\nabla_\perp \phi\right] = \frac{2\pi}{\lambda} \frac{\partial I(r_\perp, \Delta f)}{\partial z},
\]
where \(I(r_\perp, \Delta f)\) is the intensity of Lorentz micrograph, depending on magnitudes of the micrograph defocus \(\Delta f\) and the position \(r_\perp\). The subscript \(\perp\) refers to the in-plane coordinates normal to the beam direction \(z\). \(\lambda\) is the wave length of electron. In practice the derivative in the right side is approximated by using a focus series of Lorentz micrographs with the phase of electron waves traversed a length of electron. In practice the derivative in the right side is approximated by using a focus series of Lorentz micrographs with the phase of electron waves traversed a length of electron.

### 3. Results

Figure 1(a) shows a schematic view of a thin-foiled specimen prepared by a conventional FIB method; the right, left, and bottom sides of the thin-foiled area are fixed by a block that is unfixed by FIB. The \(\text{La(Fe}_{0.90}\text{Si}_{0.10})_{13}\) specimen was a thin-foil in this shape and put on a holey carbon film. As shown in the Lorentz micrograph of Fig. 1(b) (in the P phase), there is no appreciable microstructure (such as magnetic domains and/or twins) at room temperature in the viewing area, although there are many bend contours as indicated by the arrow, i.e., a typical diffraction contrast arising from Bragg reflections. When the same area is observed at a lower temperature close to \(T_C\), bright and dark lines are formed due to the appearance of magnetic domain walls, as shown in Fig. 1(c). By further cooling, the thin-foiled specimen was broken as shown in Fig. 1(d), while the magnetic domain walls are still observed clearly. It should be noted that the specimen is not broken yet in Fig. 1(c), in which the magnetic phase transition has presumably occurred in the thin-foiled area, while the phase transition is not completed yet in the block. In contrast, the specimen is completely in the F phase in Fig. 1(d). The breaking was caused by a steep volume change associated with the first-order magnetic phase transition at \(T_C\).

To explore the change in the crystallographic microstructure, we have prepared another shape of thin-foiled specimen shown in Fig. 2(a). Since the top and the right sides are free from the constraint of the block, destruction in the thin-foiled area can be avoided. The specimen was cooled from room temperature [Fig. 2(b)] to a temperature lower than \(T_C\) [Fig. 2(c)]. There is no appreciable change in the crystallographic microstructure (e.g., formation of twins and/or stacking faults) with this cubic-to-cubic transition. This feature is quite different from the case of martensitic transformations, which are the first-order transitions accompanied by a significant change in symmetry. Though \(\text{MnAs}_{10}\)\(\text{Gd}_5\left(\text{Si}_2\text{Ge}_2\right)_{11}\) and \(\text{Fe}_{49}\text{Rh}_{31}\)\(\text{Si}_{13}\) compounds are also reported to be promising for magnetic refrigerants, they exhibit the first-order magnetic phase transition with a change in the crystallographic symmetry. In such compounds, there are problems in applications to magnetic refrigerants, e.g., induce of lattice defects causes irreversibility of the transition, resulting in a reduction of magnetocaloric effects. In contrast, the \(\text{La(Fe}_{0.90}\text{Si}_{0.10})_{13}\) compounds take an advantage over the other systems because they exhibit the first-order transition without any change in the crystallographic symmetry.\(^9\)

The specimens as shaped in Fig. 2(a) have provided useful information on the magnetic domain structure as well. Figures 3(a) and (b) offer Lorentz micrographs of the \(\text{La(Fe}_{0.90}\text{Si}_{0.10})_{13}\) specimen in the P and F phases, respectively. The magnetic domain walls are clearly observed in Fig. 3(b). Some of the domain walls are indicated by paired arrowheads, whereas they are absent in the P phase [Fig. 3(a)]. The magnetization distribution in the thin-foiled specimen was obtained by solving the transport of intensity equation with respect to a focus series of the Lorentz micrographs. The result is shown in the lower panels of Fig. 3. The magnetic domains in the F phase are visualized in a color map as shown in Fig. 3(d). White arrows show
representative directions of the magnetization vectors in each domain. The color wheel (inset of the lower panels) defines directions of magnetization vectors in the color map. Since the external magnetic field (0.2 mT) is negligibly low, the magnetic flux is in principle closed within the thin-foiled area so that the demagnetization energy can be minimized. The result is similar to those in other soft magnets. On the contrary, in Fig. 3(c), there are no colored portions inside the thin-foiled area since the specimen is in the P phase.

The ferromagnetic-to-paramagnetic phase transition in La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$ was observed in situ by Lorentz microscopy. The results are provided in Figs. 4(b)–(f), each of them is a frame as captured from the TV-rate videotape. For convenience, a thermomagnetization curve of the same compound (observed in a bulk form) is supplied in Fig. 4(a). The measured temperature of the specimen may be subjected to an experimental error about ±5 K due to constraint in position of thermocouple. However, the error in magnitude of temperature hardly affects the present observation because the sharp change of magnetic domain structure can be a measure of the transition temperature. Furthermore, the sequence in temperature should be correct. Therefore, in the following discussion, it appears to be possible to regard practically the temperature, at which the magnetic domains disappear, as the Curie temperature in the observed area.

Following the results of the in situ observations, the change in the magnetic domain structure can be described as follows. In a temperature range, sufficiently lower than $T_C$ [refer to the stage as labeled I in Fig. 4(a)], the magnetic domains are stable showing no appreciable temperature dependence. On heating the specimen with a rate of 1.14 K/min., the domain configuration is modified in the temperature range II. This temperature range is likely to be quite narrow and located in the vicinity of $T_C$. The domain configuration changes stepwise in this narrow temperature range II: Fig. 4(b)$\rightarrow$Fig. 4(c)$\rightarrow$Fig. 4(d). Since the clear magnetic domains are observed in both Figs. 4(c) and 4(d), the viewing area is still in the P phase. The subsequent change is the elimination of magnetic domains as referred to the temperature range III and Fig. 4(e). The domain wall motion at $T_C$ was too fast to observe using the TV-rate video camera. For example, the bright lines as indicated by the arrows in Fig. 4(e) stem from one magnetic domain wall, which is migrating downward, and its stepwise motion is faster than the TV-rate of 1/30 second thereby the two bright lines are recorded in this frame. Once the reverse transformation to the P phase is completed, the Lorentz micrograph shows no contrasts related with magnetism in Fig. 4(f), revealing only bend contours.

4. Discussion

The Lorentz microscopy observations in Fig. 4 have disclosed the change in the magnetic domain structure with the first-order magnetic phase transition in La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$. The magnetic domains disappear instantaneously when temperature reaches $T_C$. The disappearance occurs within a time of the TV-rate (1/30 s), which corresponds to a quite small temperature change $\Delta T = 6.3 \times 10^{-4}$ K in this experiment. The observation indicates a discontinuous change in the long-range order parameter (magnetization) at $T_C$. It should be also mentioned that the disappearance of magnetic domains is accompanied by a substantial change in the volume. In fact the diffraction contrast of TEM images, e.g., position of bend contours, dramatically changes at the same time of the disappearance of magnetic domains. These are the characteristic features of the first-order phase transitions. In contrast, the second-order magnetic phase transitions show a gradual change in magnetic domain structures due to a moderate temperature dependence of magnetic moment. For example, when cooling specimens, image contrast of magnetic domain walls is pronounced in a wide range near $T_C$.

In La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$, as a consequence of magnetovolume coupling, the disappearance of magnetic domains is accompanied by a substantial volume change as ascertained by the motion of bend contours etc. The result can be explained in terms of magnetostriction. In general, volume magnetostriction $\omega$ can be expressed as

$$\omega(T) = \kappa C M^2(T),$$

where $\kappa$, $C$ and $M$ are compressibility, magnetovolume coupling constant and magnetization, respectively. Both $\omega$ and $M$ are parameters as a function of temperature. The eq. (2) indicates that a discontinuous change in magnetization yields a discontinuous change in magnetostriction.

In the Lorentz microscopy observations in Fig. 4, we have observed a faint change in the magnetic domain configuration prior to the disappearance of the magnetic domains as
referred to Figs. 4(c) and (d). At present this configuration change is not fully understood yet since we cannot rule out the artifact. e.g., this configuration change might suppose to be a consequence of the phase transition occurred already in other portions of the specimen. It is a challenging problem to discuss the fluctuations near the first-order magnetic phase transition. In situ observations of Lorentz microscopy are an effective approach to the critical phenomena of phase transitions. Further experiments are now under progress taking the advantage of the FIB method that can provide more ideal specimens to exclude the possibilities of artifact. It is also interesting to observe vector maps of magnetization as a function of temperature. For example, the vector maps may offer essential information on the nucleation sites and/or pinning sites for magnetic domains. Solving the transport of intensity equation with Lorentz micrographs is a promising approach to this essential problem. As demonstrated in Fig. 3(d), the transport of intensity equation appears to give satisfactory information on large magnetic domains. We are now testing the applicability to substantially small and/or weak ferromagnetic domains.

5. Conclusion

From the in situ observations of Lorentz microscopy on the first-order magnetic phase transition in La(Fe$_{0.895}$Si$_{0.105}$)$_{13}$ and La(Fe$_{0.90}$Si$_{0.10}$)$_{13}$, the following results are obtained.

1) Elimination of the magnetic domains occurs instantaneously at the Curie temperature when the specimen is heated from the ferromagnetic phase to the paramagnetic phase. Similarly, the magnetic domains are formed immediately at the Curie temperature with cooling from the paramagnetic phase to the ferromagnetic phase. The magnetic transition is accompanied by a significant volume change, which sometimes causes destruction of the thin-foiled specimens for TEM studies. These results are consistent with the features of the first-order magnetic phase transition.

2) There is no appreciable change in the crystallographic microstructure, e.g., formation of twins, with this first-order magnetic phase transition (cubic-to-cubic tran-

sition) despite the significant change in the lattice parameters.

3) It has been demonstrated that in situ observations of Lorentz microscopy provide useful information on the temperature dependence of magnetic domains. This technique is expected to be widely accepted in the study of phase transitions in various magnetic materials.

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REFERENCES