Local Structural Ordering in Cluster-Glass \( \text{RE}_2\text{CuSi}_3 \) (\( \text{RE} = \text{Ce} \) and \( \text{Nd} \)) compounds from HRTEM image

K. Yubuta, T. Yamamura and D. X. Li

Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

E-mail: yubuta@imr.tohoku.ac.jp

Abstract. Direct mapping of nano-domains with short-range order was presented via high-resolution transmission electron microscopy (HRTEM) on cluster-glass (CG) magnetic compounds \( \text{RE}_2\text{CuSi}_3 \) (\( \text{RE} = \text{Ce} \) and \( \text{Nd} \)) related to a hexagonal AlB\(_2\)-type structure. A new image processing technique using scanning a region of interest can be used in order to obtain the information of the structural ordering with nano-meter range. The degrees of CG on the short-range order, which shows \( \frac{1}{2} \frac{1}{2} \frac{1}{2} \) -typed superstructure spots, are consistent with those of magnetic properties. The present observations strongly support that local structures with clustering relate directly to the origin of the CG magnetic behavior in \( \text{RE}_2\text{CuSi}_3 \).

1. Introduction

Recently ternary intermetallic \( \text{R}_2\text{TX}_3 \)-type (\( \text{R} : \text{U} \) or rare earth metal, \( \text{T} : \text{d}-\text{electron transition metal and} \) \( \text{X} : \text{Si, Ge or Ga} \)) compounds have accumulated many researchers’ attention as a representative of non-magnetic atom disordered compounds. \( \text{R}_2\text{TX}_3 \) compounds with disordered AlB\(_2\)-type structure [1-3], fully ordered \( \text{U}_2\text{RuSi}_3 \)-type structure [1,4] and partially ordered \( \text{U}_2\text{RhSi}_3 \)-type structure [1,5] show spin-glass (SG), paramagnetic and ferromagnetic cluster-glass (CG) behaviors, respectively. In previous studies, magnetic properties of \( \text{Ce}_2\text{CuSi}_3 \) [6,7] and \( \text{Nd}_2\text{CuSi}_3 \) [8,9] were measured. \( \text{Ce}_2\text{CuSi}_3 \) exhibits the CG behavior below the spin freezing temperature \( T_f = 2.7 \) K. In contrast the CG feature was also observed for the almost long-range ferromagnetic ordered compound \( \text{Nd}_2\text{CuSi}_3 \) below the Curie temperature in spite of its weak effect.

It is significantly important to investigate the crystallographic features of these compounds, because of the correlation between the magnetic properties and crystal structures in order to understand the observed CG behavior. Microscopic measurements such as small angle neutron scattering (SANS), \( \mu \)SR and TEM are very useful for the local crystal structure investigation. Recently, Marcano et al. investigated a percolative process of magnetic clusters for \( \text{CeNi}_{1-x}\text{Cu}_x \) compounds by the SANS and \( \mu \)SR experiments [10-12]. From results obtained by many techniques, a phenomenological model with magnetic clusters was proposed; magnetic correlation length is about 2 nm at the cluster-glass state below \( T_f \).

In addition, HRTEM is also a powerful tool for investigating structural features in the real space by the direct observation of microstructure, especially for locally ordered arrangements of atoms. Using a filtered FFT technique for HRTEM images, we have successfully presented the domain structure of
CG Ce$_2$CuSi$_3$ and Nd$_2$CuSi$_3$ compounds showing the $\frac{1 1 1}{2 2 2}$-typed superstructure spots [13]. However, it was hard to reveal features of small domain clusters in details because of a low resolution and quantitativity of filtered HRTEM images. In this paper, we re-present the domain structure of Ce$_2$CuSi$_3$ and Nd$_2$CuSi$_3$ by using a new image processing for observed HRTEM images.

2. Experimental

Polycrystalline samples of $RE_2$CuSi$_3$ ($RE = $ Ce and Nd) were synthesized by melting stoichiometric amounts of constituent elements using an arc furnace in an argon atmosphere. The samples were then annealed at 800 °C for a week. X-ray powder diffraction patterns collected at room temperature using a diffractometer can confirm that the samples are single phases. The crystalline phases were identified by X-ray and electron diffractions. Thin samples for transmission electron microscopy (TEM) were prepared by dispersing crushed materials on holey carbon films. Electron diffraction (ED) patterns and HRTEM images were taken on TOPCON EM-002B, using an accelerating voltage of 200 kV at a resolution of 0.14 nm, and recorded using a charge coupled device (CCD) camera attached to the TEM. Image processing was performed using the ImageJ software [14].

3. Results and Discussion

No superstructure reflection cannot be detected by the X-ray diffraction measurement as reported in the previous study [13]. On the other hand, one can see clearly superstructure reflections in ED patterns of Ce$_2$CuSi$_3$ (Fig. 1(a)) and Nd$_2$CuSi$_3$ (Fig. 1(b)) compounds. ED patterns taken with incident beams parallel to the $[1 1 0]$ direction show that superstructure reflections are located at $\frac{1 1 1}{2 2 2}$-typed positions, as indicated by arrowheads with letters (s$_1$ and s$_2$). No diffuse scattering intensity indicates that the ordered phase exist in coherent with the matrix of AlB$_2$-type structure (the disordered phase). As reported in the previous studies [13,15], superstructure reflections originated from the new ordered structure, which is different from the U$_2$RuSi$_3$-type structure [4] and has a double stacking sequence of $ABAB'$, $ABAB''$ and $AB'AB''$ along the c-axis. Figures 1(c) and 1(d) show HRTEM images of the Ce$_2$CuSi$_3$ and Nd$_2$CuSi$_3$ compounds, taken with the incident beam parallel to the $[\overline{1}00]$ direction. It can be noticed at first glance that image contrasts are homogeneous in the both observed images. Although it is not be recognized to exit the ordered structure producing superstructure reflections, the Fourier diffractograms of HRTEM in Figs. 1(e) and 1(f) show weak reflection spots at $\frac{1 1 1}{2 2 2}$-type positions as indicated by arrows. To make clear the effect of the superstructure reflections, an image processing was carried out by the Fourier filtering technique using only $\frac{1 1 1}{2 2 2}$-type superstructure reflections. In the image processing, fundamental reflections were not used in order to enhance the effect of superstructure reflections. As obliquely viewing of Figs. 1(g) and 1(h), the region with symmetry of a base-centered atomic arrangement can be noticed as strong fringes. Enhanced regions correspond to those having the ordered structure. The clusters in the Ce$_2$CuSi$_3$ compound exist with sizes of about 5 nm (this length corresponds to about 7 seven unit cell of the disordered AlB$_2$-type structure). The cluster size of Nd$_2$CuSi$_3$ is much larger than that of Ce$_2$CuSi$_3$ and the region of the ordered phase is extended on a right and bottom region in Fig. 1(h). That is, domains with the ordered structure in the Nd-system were well developed rather than those of the Ce-system. This feature is consistent with the magnetic properties obtained by measurements of ac magnetic susceptibility.
Figure 1. ED patterns (a, b), HRTEM images (c, d), power spectra (e, f) and Fourier filtered images (g, h) of the Ce$_2$CuSi$_3$ (left) and Nd$_2$CuSi$_3$ (right) compounds, taken with the incident beams parallel to the $\langle 1\bar{1}0 \rangle$ direction. The image processing was carried out by Fourier filtering technique, using superstructure $\frac{111}{222}$-typed reflections.

Although the Fourier filtered images give us significantly important information for the clustering, a spatial resolution and quantitativity of the ordering in the processed images were too low to discuss features of the clustering in details. Thus, in order to make the distribution of ordered domains clarify furthermore, new image analysis was carried out. Figure 2 illustrates a scheme of the image processing...
in this study. Each power spectrum was calculated from a region of interest that moves scanning on the image. Subsequently the intensity of an area which corresponds to the diffraction spot in the reciprocal space was measured. A size and a gradation of observed HRTEM images were 2048 × 2048 pixel$^2$ (≈ 45.1 × 45.1 nm$^2$) and 16 bit gray scale, respectively. In the narrow regions, it can be postulated that thickness of samples is constant in the each sample. Power spectra were obtained from a square region having a size of 512 × 512 pixel$^2$ (≈ 11.3 × 11.3 nm$^2$). A step width in the scanning of the square region was 4 pixel (≈ 0.1 nm). Intensity of satellite and fundamental spots, $I_s$ and $I_f$, was estimated as an integrated density of oval regions after background subtraction. Diffraction spots, $\{111, \overline{111}, 222, \overline{222}\}$, and 001, were chosen as satellite ones $s_1, s_2$ and fundamental one $f$, respectively, in Fig. 2(b). The degree of the structural ordering was defined as $I_s / I_f$ in order to minimize dynamical effect in the real imaging. The present imaging procedure is considered as a kind of the scanning dark-field imaging method. It is believed that obtained maps were relatively credible to compare results between Ce- and Nd-compounds.

![Figure 2](image-url)

**Figure 2.** Schematic illustration of image analysis. A power spectrum (b) is performed from a gray square in (a) having a size of 512 × 512 pixels$^2$.

Figure 3 shows maps of the degree of the structural ordering, (a, b) $I_{s1} / I_f$, (c, d) $I_{s2} / I_f$ and (e, f) $(I_{s1} + I_{s2}) / 2I_f$, for the Ce$_2$CuSi$_3$ (left) and Nd$_2$CuSi$_3$ (right) compounds from Figs. 1(c) and 1(d). The high ratio of $I_s / I_f$ indicates that the high structural ordering occurs in the corresponding region. It can be recognized that a fine distribution of the clustering, which does not appear in Figs. 1(g) and 1(h), exist. The dispersed domain structure can be noticed more directly by the scanning-microscopic method compared to the Fourier filtering technique. From a detailed analysis, it was found in both systems that enhanced regions for $s_1$ and $s_2$ diffraction spots are slightly different, i.e., the mirror symmetry was broken. It is difficult for conventional enhanced FFT images as shown in Figs. 1(g) and 1(h) to find out the difference. The reason of the characteristic was considered that complex short-range order, rather than long-range order, originated from. In the other words, this result is due to three types of stacking sequences along the $c$-axis, namely, $ABAB'$, $ABAB''$ and $AB'AB''$ for the ordered structure [13,15]. A size of clusters in the Ce-compound is estimated as 2 ~ 3 nm, on the other hand, that is more than 30 nm in the Nd-one. Apparently, larger ferromagnetic clusters are developed in the Nd-system. The topological feature is consistent with the magnetic properties reported in the previous studies [7,9].

It is demonstrated that the scanning dark-field imaging method is useful for investigating sscale ordered domain structures. A HAADF-STEM observation, which is generally interpreted as chemical atomic number $Z$-contrast imaging, is an effective method especially for a compositional modulation. On the other hand, because the frameworks were constructed by heavy $RE$ atoms in the present compounds, it is difficult to detect the chemical ordering between relative light Cu and Si atoms by the HAADF-STEM. We consider that the present image processing is a suitable method for clearing the existence of the coherently short-range ordered domain structure in nano-meter order.
Figure 3. Maps of the degree of the structural ordering from observed HRTEM images (Figs. 1(c) and (d)) of the Ce$_2$CuSi$_3$ (left) and Nd$_2$CuSi$_3$ (right) compounds. Top, middle and bottom images are obtained using $s_1$, $s_2$ and $s_1+s_2$ satellite spots of Figs. 1(a) and (b), respectively. Red and blue pixels indicate strong and weak ordered regions.
4. Conclusions
We present the inhomogeneous distribution of ordered domains of the $RE_2CuSi_3$ ($RE=$Ce and Nd) compounds by using scanning microscopic processing for HRTEM images. Obtained mappings show more fine distributions of the ordered structure rather than those of the conventional FFT processing. In addition, mappings can exhibit the degree of the structural ordering more precisely. On the basis of the new image processing, it could be concluded that the observed domain structures are strongly related to an origin of the CG behavior of the $RE_2CuSi_3$ compounds.

References
[1] Chevalier B, Pöttgen R, Darriet B, Gravereau P and Etourneau J 1996 J. Alloys Compd. 233 150
[2] Pöttgen R and Kaczorowski D 1993 J. Alloys Compd. 201 157
[3] Kaczorowski D and Noël H 1993 J. Phys.: Condens. Matter 5 9185
[4] Pöttgen R, Gravereau P, Darriet B, Chevalier B, Hickey E and Etourneau J 1994 J. Mater. Chem. 4 463
[5] Li DX, Dönni A, Kimura Y, Shiokawa Y, Homma Y, Haga Y, Yamamoto E, Honma T and Onuki Y 1999 J. Phys.: Condens. Matter. 11 8263
[6] Hwang JS, Lin KJ and Tien C 1996 Solid State Commun. 100 169
[7] Li DX, Shiokawa Y, Nimori S, Haga Y, Yamamoto E, Matsuda TD and Onuki Y 2003 Physica B 329-333 506
[8] Tien C, Luo L and Hwang JS 1997 Phys. Rev. B 56 11710
[9] Li DX, Zhao X, Nimori S, Koyama K and Shiokawa Y 2009 J. Phys.: Condens. Matter 21 026006
[10] Marcano N, Espeso JI, Gómez Sal JC, Rodríguez Fernández J, Herrero-Albillos J and Bartolomé F 2005 Phys. Rev. Lett. 71 134401
[11] Marcano N, Gómez Sal JC, Espeso JI, De Teresa JM, Algarabel PA, Paulsen C and Iglesias JR 2007 Phys. Rev. Lett. 98 166406
[12] Marcano N, Gómez Sal JC, Espeso JI, Fernández Barquín L and Paulsen C 2007 Phys. Rev. B 76 224419
[13] Yubuta K, Yamamura T and Li DX 2009 Solid State Commun. 149 286
[14] http://rsb.info.nih.gov/ij
[15] Yubuta K, Yamamura T and Shiokawa Y 2006 J. Phys.: Condens. Matter 18 6109