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Direct observation of the microstructure in cluster glass compound U_2IrSi_3

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Abstract

We have examined the structure of a U_2IrSi_3 compound exhibiting ferromagnetic cluster glass behaviour by means of electron diffraction observation and high-resolution electron microscopy. The structure of U_2IrSi_3 has been proposed as a new one of the U_2RuSi_3-type with a short-range ordered double stacking sequence of the U_2RuSi_3-type structure along the *c*-axis, and long-range ordered atomic arrangements in the *a*–*b* plane. The calculated patterns reproduce the characteristic features of observed electron patterns well. The Fourier-filtered high-resolution image clearly exhibits a micro-domain structure, which is considered to relate directly to the origin of the observed cluster glass behaviour in U_2IrSi_3.

1. Introduction

Uranium ternary compounds U_2XSi_3 exhibit a variety of magnetic properties including spin glass behaviour (X = Pt [1–5], Pd [3, 4, 6] and Au [3, 4]), paramagnetic ground state (X = Fe [3–5, 7–9], Ru [3, 4, 9, 10] and Os [3, 4]), and ferromagnetic cluster glass behaviour (X = Rh [3, 4, 11] and Ir [3, 4, 12]). Recently these magnetic properties have revealed a significant relationship with their crystal structures as listed in table 1. The structure of the spin glass phases (X = Pt, Pd and Au) has AlB_2-type structure, perfectly disordered with X and Si atoms at the same crystallographic sites (B site). This randomness on the same crystallographic site (B site of AlB_2-type structure) results in the competition between ferromagnetic and anti-ferromagnetic U–U exchange interactions, and thus causes the frustration of U magnetic moments. On the other hand, the paramagnetic phase (X = Fe, Ru and Os) has U_2RuSi_3-type structure with ordered arrangement of X and Si atoms [4]. For ferromagnetic cluster glass phase, Chevalier *et al* have suggested that the structure of U_2RhSi_3 has an orthorhombic cell with partially ordered arrangement of Rh and Si atoms at B site [4]. Generally, magnetic properties of these ternary compounds are strongly influenced by the nature of transition metal elements. In addition, the atomic arrangements must be important for understanding the spin glass behaviour.

Table 1. Magnetic properties and crystal structures appearing in the literatures for U_2XSi_3 compounds.

Fe PM / FO			
Ru PM / FO	**Rh** CG / PO	**Pd** SG / DO	
Os PM / FO	**Ir** CG / DO†,PO§	**Pt** SG / DO	**Au** SG / DO

Magnetic properties (symbols at upper left)

PM : paramagnetic phase

SG : spin glass phase

CG : ferromagnetic cluster glass phase

Crystal structures (symbols at lower right)

FO : full ordered phase, U_2RuSi_3-type

PO : partial ordered phase, U_2RhSi_3-type

DO : disordered phase, AlB_2-type

†: ref. [4]

§: this study

Recently, another example of ferromagnetic cluster glass was found in the U_2IrSi_3 compound with a spin freezing temperature $T_f = 10.5$ K by Li *et al* [12]. The up-shift of the ac susceptibility peak with increasing frequency, the irreversibility in temperature dependence of dc magnetization, the long-time magnetic relaxation even in applied field much larger than the coercive field, the small jump in initial magnetization curve, and the small specific heat anomaly, which contains a very small amount of magnetic entropy, are typical features characteristic of the ferromagnetic cluster glass behaviour. However, the x-ray powder diffraction measurement seems to show the AlB_2-type pattern structure for U_2IrSi_3, and no additional diffraction line characteristic of superstructure was observed. Comparing these results with those reported for U_2RhSi_3, we consider that a certain kind of disorder structure should also exist in the U_2IrSi_3 compound, although this could not be confirmed by x-ray powder diffraction measurement.

Electron diffraction and high-resolution electron microscopy are powerful tools for investigating the structure both in real and reciprocal space, and especially for investigating locally disturbed arrangements of atoms. In this work, the atomic arrangements in the U_2IrSi_3 compound are studied by electron diffraction and high-resolution electron microscopy. Based

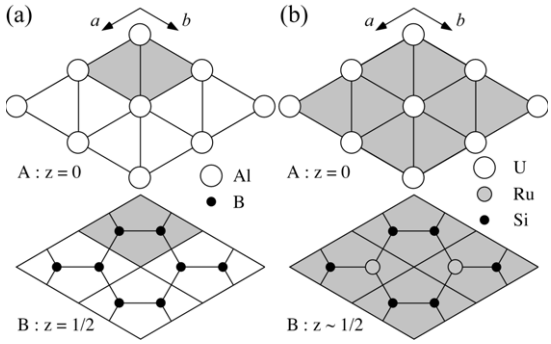

Figure 1. Atomic arrangements in (a) AlB_2-type and (b) U_2RuSi_3-type structures. The shaded areas indicate unit cells.

on the obtained results, we propose a structural model that could explain the observed cluster glass behaviour observed in the U_2IrSi_3 compound.

2. Experimental details

A polycrystalline sample of U_2IrSi_3 was synthesized by melting stoichiometric amounts of constituent elements using an arc furnace in an argon atmosphere. The purities of starting materials are 3 N for U and 6 N for Ir and Si. Weight loss in the melting process is smaller than 0.2 wt%. The sample was then annealed at 800 °C for a week. An x-ray powder diffraction pattern collected at room temperature using a diffractometer can confirm that the sample is a single phase.

Thin samples for transmission electron microscopy were prepared by dispersing crushed materials on holey carbon films. Electron diffraction patterns and a high-resolution image were obtained using a 400 kV electron microscope (JEM-4000FXII) at room temperature.

3. Results and discussion

It has been investigated that some U_2XSi_3 (X = Pd, Pt, Au) compounds have an AlB_2-type structure from x-ray powder diffraction patterns [3, 4]. Figure 1(a) shows the crystal structure of the AlB_2-type structure (space group $P6/mmm$). In the U_2XSi_3 compounds, U atoms occupy the Al site, and X and Si atoms randomly occupy the B sites with a ratio of X/Si = 1/3, respectively. On the other hand, U_2RuSi_3 and U_2OsSi_3 compounds show ordered structures with a two-dimensional network [4, 10]. The structure of U_2RuSi_3 has been investigated by single-crystal x-ray diffraction study [10]. Figure 1(b) shows the crystal structure of U_2RuSi_3 (the space group $P6/mmm$). The lattice parameters are $a = 8.145$ Å and $c = 3.8496$ Å. Ru and Si atoms are on the $2d$ (1/3, 2/3, 1/2) and the $12o$ split position (x, $2x$, 0.4433) with $x = 0.166$ with the occupation probability of 0.5.

Figure 2 shows an x-ray diffraction pattern of the U_2IrSi_3 compound (a), and calculated patterns from the AlB_2-type (disordered phase) (b) and U_2RuSi_3-type (ordered phase) structures (c), respectively. The x-ray powder diffraction pattern of figure 2(a) shows that the U_2IrSi_3 compound has a hexagonal AlB_2-type structure with lattice parameters of $a_{XPD} = 4.090$ Å and $c_{XPD} = 3.954$ Å, without other phases.

Figure 3 shows electron diffraction patterns of the U_2IrSi_3 compound ((a), (b)), taken with incident beams along the [001] (a) and $[\bar{1}\bar{1}0]$ (b) directions, with those of U_2PdSi_3 ((c), (d))

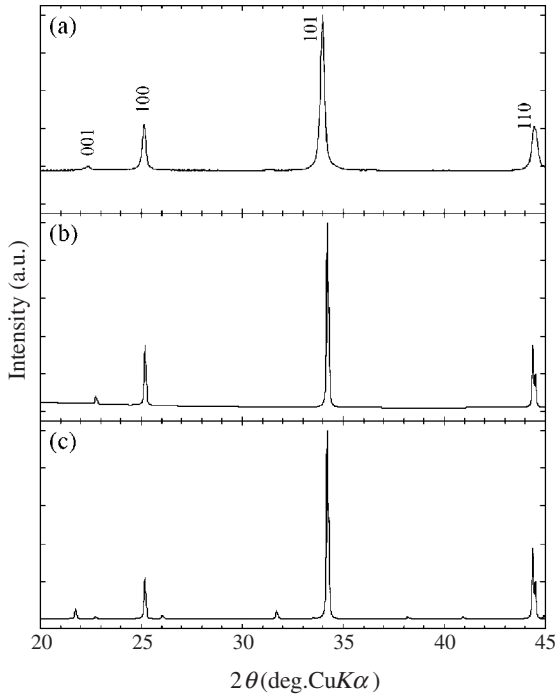

Figure 2. (a) X-ray diffraction patterns observed from the U_2IrSi_3 compound, (b) calculated from the AlB_2-type and (c) calculated from U_2RuSi_3-type structures. Reflections are indexed by the AlB_2-type structure.

and U_2FeSi_3 ((e), (f)) compounds. The electron diffraction patterns of U_2PdSi_3 in figures 3(c) and (d) can be explained by the hexagonal AlB_2-type structure with lattice parameters of $a = 4.083$ Å and $c = 3.932$ Å. On the other hand, the electron diffraction patterns of figures 3(e) and (f) for U_2FeSi_3 show the existence of superlattice reflections, which indicate doubling of the lattice parameter along the a-axes. Yamamura *et al* [5] pointed out that the structure of U_2FeSi_3 can be explained as a U_2RuSi_3-type structure, among the various derivative structures related to the AlB_2-type structure in the *Bärnighausen* tree [13]. The lattice parameters were determined as $a = 8.003$ Å and $c = 3.854$ Å from a powder x-ray diffraction pattern.

On the other hand, the diffraction pattern of U_2IrSi_3 in figure 3(b) shows diffuse streaks parallel to the c^*-axis. The diffuse streaks have maximum intensities at 1/2 1/2 1/2-type positions, as indicated by arrowheads. This observation shows the existence of a fundamental long-range ordered structure with 1/2 1/2 1/2-type superlattice reflections, and plate-like micro-domains with long-range ordering of the fundamental structure in the a–b plane and short-range ordering along the c-axis. It is possible that this plate-like structure is an origin of the cluster glass phase.

The fundamental ordered structure with the 1/2 1/2 1/2-type superlattice reflections can be considered to be different from the U_2RuSi_3-type structure and to have a double stacking sequence of ABAB′ along the c-axis. Figure 4(a) shows a model of the fundamental structure. In the model, the arrangement of Ir and Si atoms on the B plane is the same as that of Ru and Si atoms on the B plane in figure 1(b), and the atomic arrangement on the B′ plane is

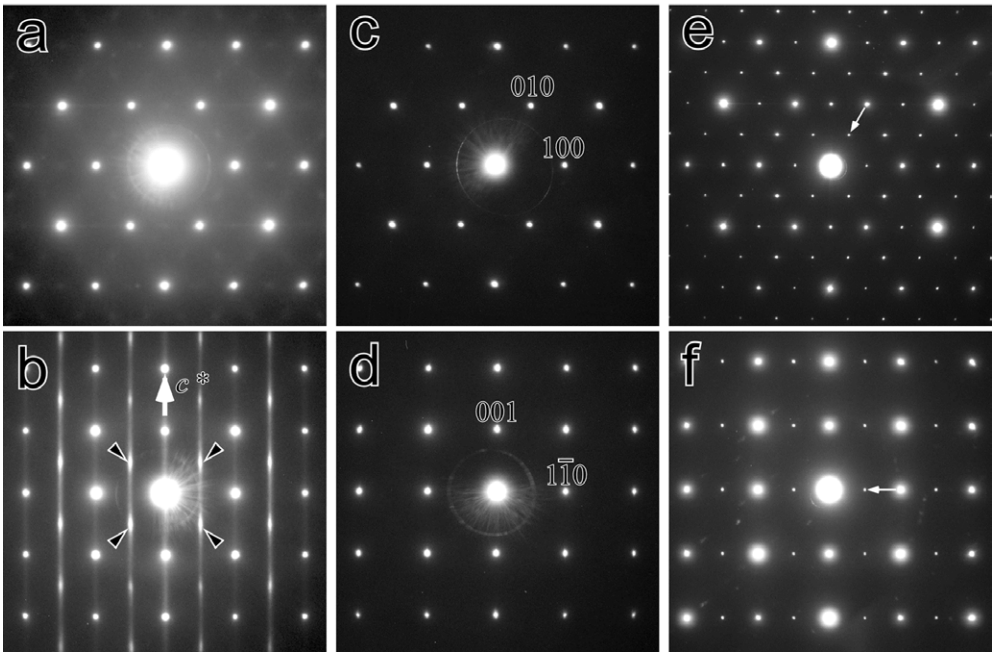

Figure 3. (a), (b) Electron diffraction patterns of the U_2IrSi_3, (c), (d) U_2PdSi_3, and (e), (f) U_2FeSi_3 compounds, taken with the incident beams along the [001] ((a), (c), (e)) and [$\bar{1}\bar{1}$0] ((b), (d), (f)) directions. In (b), notice the appearance of 1/2 1/2 1/2-type reflections indicated with arrowheads, and streak-like diffuse scattering parallel to the c^*-axis. Small arrows in (e) and (f) indicate the ordered reflections with $a_{U_2RuSi_3} = 2a_{AlB_2}$.

formed by displacing that of the B plane with a vector indicated by an arrow. In the same way, the B″ plane of figure 4 can be formed. As a result, three types of stacking sequences, namely ABAB′, ABAB″ and AB′AB″ for the fundamental structure can be considered. The diffuse streaks along the c^*-axis in the electron diffraction pattern of figure 3(b) probably result from short-range ordering for those three stacking sequences. In figure 4(b), the structure projected to the [110] direction for the layer sequence of ABAB′ is shown as an example. It is clear that Ir/Si sites have centred symmetry. We have calculated electron diffraction patterns to confirm the structural model. Figure 4(c) shows an electron diffraction pattern calculated kinematically from the present model, assuming that it is taken with the incident beam along the [110] direction. This calculated pattern reproduces the observed intensity distribution with the 1/2 1/2 1/2-type superlattice reflections well, as indicated with an arrowhead in figure 3(b).

Figure 5(a) shows a high-resolution image of the U_2IrSi_3 compound, taken with the incident beam parallel to the [$\bar{1}\bar{1}$0] direction. Bright dots correspond to U sites, and weak dots at face-centred positions of the bright dots are Ir/Si sites. It is not easy to see a modulated structure producing diffuse scatterings from the observed image, but the Fourier diffractogram of figure 5(b) shows weak diffuse streaks with strong intensities at 1/2 1/2 1/2-type positions. To make clear the effect of the diffuse streaks, image processing was carried out by the Fourier filtering technique, using only superstructure reflections and diffuse streaks without fundamental reflections. Figure 5(c) shows the Fourier filtered image of the observed high-resolution image. In the filtered image, the image contrasts, i.e. periodicities of atomic arrangements, originated from the superstructure reflections and diffuse streaks were

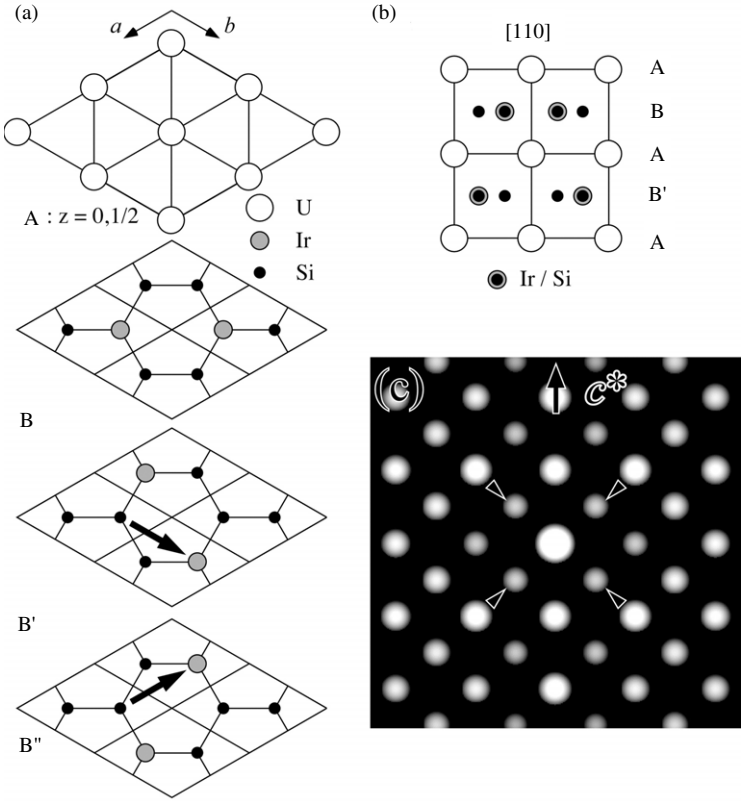

Figure 4. (a) Structural model for U_2IrSi_3, (b) the projected structure along the [110] direction and (c) the calculated diffraction pattern of (b). In (b), the layer sequence is ABAB′. As indicated with arrowheads in (c), 1/2 1/2 1/2-type superlattice reflections are well reproduced.

emphasized. Obliquely viewing figure 5(c) along the horizontal direction, one can recognize thin ordered regions with an average length of about 100 Å along the $[1\bar{1}0]$ direction. (This length corresponds to about 14 unit cells of the AlB_2-type structure.) That is, the thin ordered regions are regarded as the origin of superstructure reflections and diffuse streaks and consist of the atomic arrangements indicated in figure 4(a).

The structure of U_2IrSi_3 can be regarded as a new one related to the AlB_2- and U_2RuSi_3-type structures. Although the electron diffraction and high-resolution images were observed at room temperature, it might be concluded that the observed micro-domains in U_2IrSi_3 are related to the magnetic properties, i.e. ferromagnetic cluster glass.

4. Conclusion

We have studied the structure of the U_2IrSi_3 compound by electron diffraction and high-resolution observations. Observed diffraction patterns show diffuse streaks with maximum intensities at 1/2 1/2 1/2-type positions along the c^*-axis, and the high-resolution image indicates plate-like micro-domains extended along the *a*–*b* plane. The long-range ordering of atoms along the *a*–*b* plane is similar to that of the U_2RuSi_3-type structure, and short-range ordering along the *c*-axis results from disordering of the stacking sequence of ordered

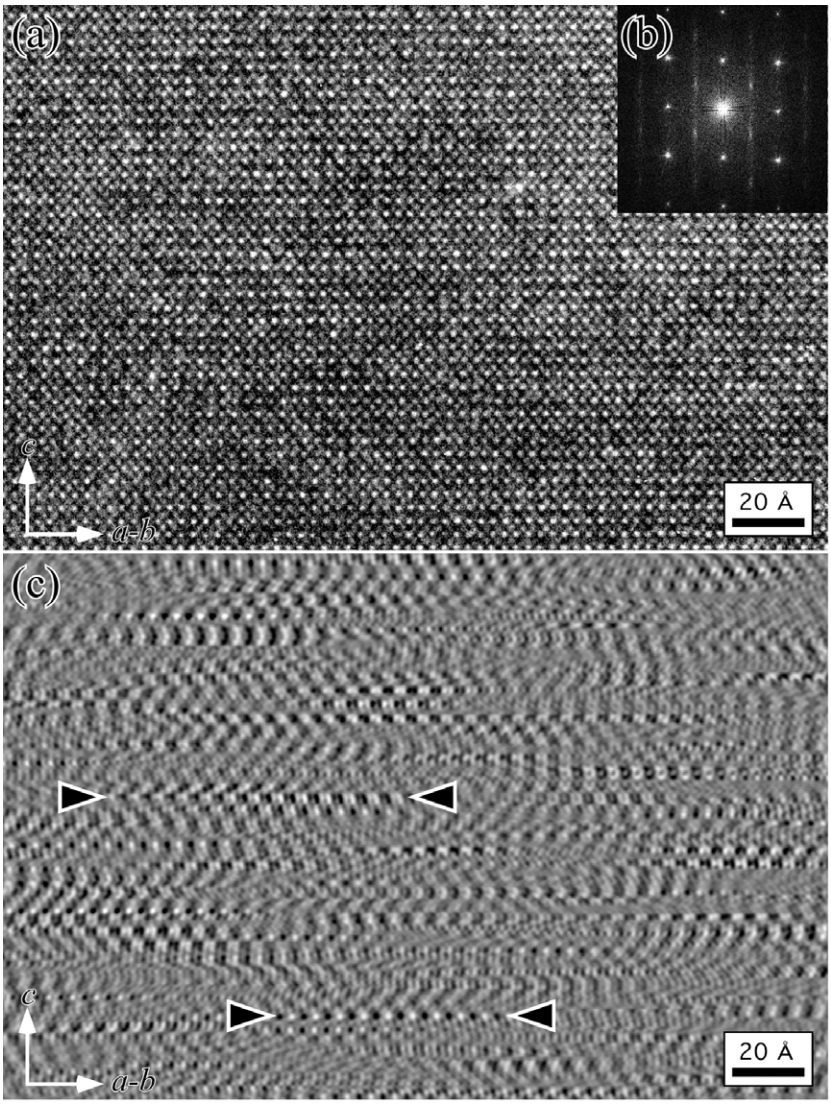

Figure 5. (a) High-resolution image of the U_2IrSi_3 compound, taken along the $[\bar{1}\bar{1}0]$ direction. (b) and (c) are a Fourier diffractogram and Fourier filtered image of (a), respectively. Pairs of arrowheads in (c) indicate micro-domain structures.

arrangements of the *a–b* plane. It might be concluded that the observed micro-domains are related to an origin of the cluster glass behaviour of the U_2IrSi_3 compound.

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References

[1] Geïbel C, Kämmerer C, Göring E, Moog R, Sparn G, Henseleit R, Cordier G, Horn S and Steglich F 1990 *J. Magn. Magn. Mater.* **90/91** 435
[2] Sato N, Kagawa M, Tanaka K, Takeda N, Satoh T and Komatsubara T 1992 *J. Magn. Magn. Mater.* **108** 115
[3] Pöttgen R and Kaczorowski D 1993 *J. Alloys Compounds* **201** 157
[4] Chevalier B, Pöttgen R, Darriet B, Gravereau P and Etourneau J 1996 *J. Alloys Compounds* **233** 150
[5] Yamamura T, Li D X, Yubuta K and Shiokawa Y 2006 *J. Alloys Compounds* **408–412** 1324
[6] Li D X, Shiokawa Y, Homma Y, Uesawa A, Dönni A, Suzuki T, Haga Y, Yamamoto E, Honma T and Onuki Y 1998 *Phys. Rev.* B **57** 7434
[7] Pinto M D 1966 *Acta Crystallogr.* **21** 999
[8] Kaczorowski D and Noël H 1993 *J. Phys.: Condens. Matter* **5** 9185
[9] Takeda N and Ishikawa M 1998 *J. Phys. Soc. Japan* **67** 1062
[10] Pöttgen R, Gravereau P, Darriet B, Chevalier B, Hickey E and Etourneau J 1994 *J. Mater. Chem.* **4** 463
[11] Li D X, Dönni A, Kimura Y, Shiokawa Y, Homma Y, Haga Y, Yamamoto E, Honma T and Onuki Y 1999 *J. Phys.: Condens. Matter* **11** 8263
[12] Li D X, Nimori S, Shiokawa Y, Haga Y, Yamamoto E and Onuki Y 2003 *Phys. Rev.* B **68** 172405
[13] Hoffmann R D and Pöttgen R 2001 *Z. Kristallogr.* **216** 127