

Residual short-range order in the heavy fermion compound CeInCu₂

ISAO TAKAHASHI,^{a*} AKIKO KAGAYAMA,^b GENDO OOMI,^b YOSHICHIKA ONUKI^c AND TAKEMI KOMATSUBARA^d

^aAdvanced Research Center of Science (ARCS) of Kwansei Gakuin University, Nishinomiya 662, Japan, ^bFaculty of Engineering, Kumamoto University, Kumamoto 860, Japan, ^cInstitute of Material Science, University of Tsukuba, Ibaraki 305, Japan, and ^dDepartment of Physics, Tohoku University, Sendai 980, Japan.

E-mail: suikyo@kwansei.ac.jp

(Received 8 January 1998; accepted 21 July 1998)

Abstract

By using the X-ray diffraction technique, residual short-range order was detected in CeInCu₂, cerium dicopper indium, which is known to be a heavy fermion compound. In spite of the long-range order of this substance, diffuse scattering exhibiting short-range order was observed at room temperature. The correlation parameters obtained showed that an incorrectly occupied lattice site has a tendency to gather atoms of different species at the neighboring sites along the $\langle 111 \rangle$ directions. Thus, the disordered region would form a cluster composed of several disordered atoms. Furthermore, a chain-type correlation which has a period of 20–23 Å along the same directions was indicated. The superstructure-like feature of the disordered atoms hardly increases the residual resistivity. It is consistent with the behavior of the residual resistivity under high pressure.

1. Introduction

CeInCu₂ is classified as a heavy fermion compound having a large specific heat coefficient, $\gamma \simeq 1.2 \text{ J mol}^{-1} \text{ K}^{-2}$ at 1 K, indicating a large effective mass (Lahouie *et al.*, 1987; Onuki *et al.*, 1987). The electrical resistivity increases gradually with decreasing temperature, but it decreases below 25 K owing to the coherent scattering of conduction electrons. CeInCu₂ has been regarded as a special substance by researchers eager to obtain an insight into the effect of a crystalline electric field on physical properties, since the lattice type is cubic and the crystal structure is fairly simple [MnAlCu₂-type Heusler structure, $a = 6.79$ (1) Å], in contrast with other heavy fermion compounds which are mostly characterized by lower crystallographic symmetry (Kagayama *et al.*, 1991). It is also well known that the Heusler-type alloy includes some kind of disorder in the crystal lattice sites. In fact, slight structural disorder has already been reported for CeInCu₂. According to Takayanagi *et al.* (1988), $\sim 10\%$ of Ce atoms are exchanged by In atoms and *vice versa* [the long-range order (LRO) parameter $S \equiv (\text{probability of finding a Ce atom at a Ce site}) - (\text{probability of finding an In atom at a Ce site}) \simeq 0.8$].

Therefore, the structural disorder observed at room temperature has been thought to be the origin of several peculiar electrical properties of this substance at low temperature, assuming that the disorder still exists at low temperature:

(a) large residual resistivity ρ_0 of $\sim 80 \mu\Omega \text{ cm}$ (Onuki *et al.*, 1987; Kagayama *et al.*, 1991);

(b) an extremely small coefficient of the T^2 term in the resistivity, $0.8 \mu\Omega \text{ cm K}^2$ (Kagayama, 1995), compared with the typical heavy fermion compound CeAl₃, which has a value two orders of magnitude larger (Andres *et al.*, 1975).

However, further study to provide conclusive proof has not yet been reported. In this paper details of the structural disorder in CeInCu₂ investigated by precise X-ray diffraction measurements are presented.

2. Experimental and results

A single crystal of CeInCu₂ was grown by the Czochralski crystal-pulling method. A surface corresponding to the (001) plane with a $6 \times 6 \text{ mm}^2$ area was polished. The X-ray diffraction experiments were performed at the Photon Factory at the National Laboratory for High Energy Physics (PF, KEK). A four-circle diffractometer installed at the beamline 4C was used. The wavelength of the monochromated X-ray beam was 1.0 Å and all the measurements were performed at room temperature.

Intensities and peak widths of several Bragg reflections were measured so as to check the crystallinity and to determine the LRO parameter of our sample using the method of Takayanagi *et al.* (1988). The 006 and 339 Bragg reflections were corrected for Lorentz-polarization effects. From the ratio of these reflections, the LRO parameter S was evaluated as 0.76, which almost agrees with the value given above.

Diffuse scattering was searched for in a parallelepipedic region which has eight corners at 002, 102, 012, 112, 003, 103, 013 and 113 in reciprocal space. Consequently, rod-shaped diffuse scattering was found in the (110) plane; it was confirmed in another equivalent rectangular area with corners at 002, $\bar{1}12$, $\bar{1}13$ and 003 in

reciprocal space. Fig. 1 shows the observed intensity distribution in the (110) plane. The narrow rod-shaped diffuse scattering emanates from 002 and reaches 113. Except for this rod-shaped diffuse scattering lying along the $\langle 111 \rangle^*$ direction, no distinct diffuse scattering was seen in the region searched. In Fig. 1 three spots around $\frac{1}{2}, \frac{1}{2}, 2.05$, $0, 0, 2.65$ and $1, 1, 2.7$ are seen. From measurements close to these points it was concluded that these spots are not diffuse scattering; we believe that some are Bragg reflections generated by the $\lambda/3$ component of the incident beam.

Electrical resistance was measured at high pressure using a standard four-probe method. The hydrostatic pressure was generated by a cubic anvil press having an anvil face of $4 \times 4 \text{ mm}^2$. The pressure-transmitting medium was a mixture of Fluorinert FC70 and FC77.

3. Analysis

The intensity distribution between 002 and 113 in reciprocal space is plotted in Fig. 2. The rod-shaped diffuse scattering shows several broad peaks between these points. Thus, the diffuse scattering could not be explained by thermal diffuse scattering (TDS) alone, which usually exhibits maxima at reciprocal lattice points, but it manifests short-range order in the almost ordered phase of CeInCu₂. Therefore, it may be regarded as residual short-range order surviving in the ordered phase where the Ce and In sites are distinctly defined. The peaks between the reciprocal lattice points remind us of satellite scattering from a modulated structure characterized by a long period relative to the period of the basic structure. However, the broad peaks shown in Fig. 2 do not indicate a complete modulated structure. We believe that the structural disorder is likely to indicate a periodic feature. If the disorder has such a feature, the period should be $\sim 20\text{--}23 \text{ \AA}$, as readily estimated from the position of the peaks.

Since the crystal structure of CeInCu₂ is face-centered cubic, the structure can be regarded as an infinite

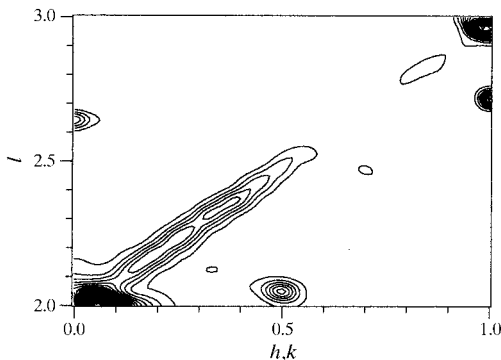


Fig. 1. Equal-intensity lines in the (110) plane in reciprocal space. Rod-shaped diffuse scattering is seen from the 002 point to the 113 point of the reciprocal lattice.

repetition of a Ce plane and an In plane sandwiched by Cu planes, if we project the crystal structure onto an axis along the $[111]$ direction. Since the rod-shaped diffuse scattering was observed to be quite narrow in a plane normal to the $[111]^*$ direction in reciprocal space, the disordered atoms are thought to be positioned randomly within each Ce and In plane. Therefore, we can focus on the correlation among these planes (= correlation along the $[111]$ direction) without further consideration of any correlation within each Ce plane and within each In plane. In the remainder of this paper a one-dimensional chain model which consists of Ce (= Ce sites), Cu (= Cu sites) and In planes (= In sites) is considered, and the intensity distribution along the $[111]^*$ direction is analyzed. The intensity of the observed diffuse scattering is represented by one index h ($0 < h < 1$) as $I(h, h, h + 2)$. Thus, it is denoted briefly as $I(h)$.

$I(h)$ is a function of several correlation parameters, $p_{\alpha}^A B_{\beta}(n)$, which is the probability of finding atom β at the B site of the n th neighbor when atom α is occupied on the A site located at the origin (at $n = 0$). To analyze the diffuse scattering we have to consider at least four independent correlation parameters: $p_{\text{Ce Ce}}^{\text{Ce In}}(n)$, $p_{\text{In Ce}}^{\text{Ce Ce}}(n)$, $p_{\text{In In}}^{\text{In In}}(n)$ and $p_{\text{In Ce}}^{\text{In In}}(n)$. Then, $I(h)$ is expressed as

$$I(h) = k\{f_{\text{Ce}} - f_{\text{In}}\}^2 \left[\sum_{n=0}^{\infty} A_n \cos(2\pi hn) + 2 \sum_{n=0}^{\infty} B_n \{\cos[2\pi h(n + \frac{1}{2})]\} / \{f_{\text{Ce}} - f_{\text{In}}\} \right], \quad (1)$$

where the coefficients A_n and B_n are defined as

$$A_n = 2x(\text{Ce})x(\text{In}) - \{x(\text{In})p_{\text{In Ce}}^{\text{Ce Ce}}(n) + x(\text{Ce})p_{\text{In In}}^{\text{In In}}(n)\}, \quad (2)$$

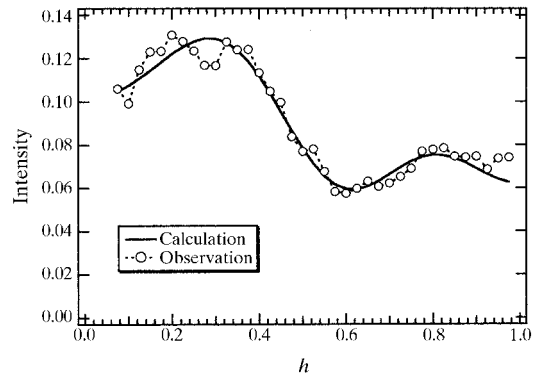


Fig. 2. The intensity distribution along the line $h, h, h + 2$ in reciprocal space. Broad peaks are seen at $h \simeq 0.2, 0.35$ and 0.8 . The solid curve is the intensity calculated using the parameters listed in Table 1. The units of the intensity are arbitrary. The measured intensity around $0.2, 0.2, 2.2$ was ~ 18 counts per s, which was approximately three times as large as the background intensity.

$$B_n = f_{\text{Ce}}x(\text{In})\{x(\text{In}) - p_{\text{In}}^{\text{Ce}}x_{\text{Ce}}(\text{In})(n)\} - f_{\text{In}}x(\text{Ce})\{x(\text{Ce}) - p_{\text{Ce}}^{\text{In}}x_{\text{In}}(\text{Ce})(n)\}. \quad (3)$$

$x(\text{Ce})$ and $x(\text{In})$ represent the average ratio of finding a Ce atom at a Ce site and that of finding an In atom at a Ce site, respectively. f_{Ce} and f_{In} are the atomic form factors of Ce and In, respectively. Although the above equations seem to be complicated, significant features can easily be seen:

- (i) if $f_{\text{Ce}} = f_{\text{In}}$, then $I(h) = 0$;
- (ii) if $x(\text{In}) = p_{\text{In}}^{\text{Ce}}x_{\text{Ce}}(\text{In})(n) = p_{\text{In}}^{\text{In}}x_{\text{In}}(\text{Ce})(n)$ and $x(\text{Ce}) = p_{\text{Ce}}^{\text{In}}x_{\text{In}}(\text{Ce})(n) = p_{\text{Ce}}^{\text{Ce}}x_{\text{Ce}}(\text{In})(n)$, then $I(h) = 0$.

Whilst (i) is obvious (ii) indicates that the diffuse scattering vanishes when the correlation vanishes.

We evaluated A_n and B_n from numerical integration, $\int_0^1 I_{\text{obs}}(h)\cos(2\pi hn)dh$ and $\int_0^1 I_{\text{obs}}(h)\cos(2\pi h(n + \frac{1}{2}))dh$. The value of A_0 was fixed as $2x(\text{Ce})x(\text{In})$. The solid curve in Fig. 2 is the calculated intensity using the coefficients listed in Table 1. We can see that an intrinsic part of the observed intensity distribution can be satisfactorily reproduced by a small number of coefficients.

4. Discussion

A_n and B_n rapidly approach zero when n increases. This indicates that the correlation in the structural disorder is not so dominant between the sites beyond the second neighbors. It is not easy to evaluate the correlation parameters from the values of the coefficients, since there are four unknown parameters for only two coefficients. However, $p_{\text{Ce}}^{\text{In}}x_{\text{In}}(\text{Ce})(0)$ is expected to have a value close to one. Hence, we can evaluate $p_{\text{In}}^{\text{Ce}}x_{\text{Ce}}(\text{In})(0)$ as ~ 0.84 from the B_0 value obtained. This indicates that $\sim 84\%$ of an In site is occupied by a Ce atom when the adjacent Ce site is occupied by an In atom along the

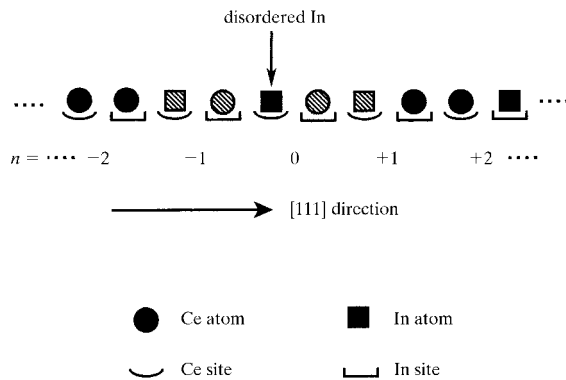


Fig. 3. Schematic representation of the disordered cluster in CeInCu_2 along the $[111]$ direction. The Cu sites are not drawn for clarity. When a Ce site is occupied by an In atom (represented by the square at $n = 0$), the probability of finding Ce atoms in the adjacent In sites is 0.84 (hatched circle at $n = 0$ and -1). Such disorder is also expected at the sites indicated by the hatched In atoms at $n = -1$ and $+1$.

Table 1. The coefficients of equation (1) obtained by numerical integration

n	A_n	B_n
0	0.2262	0.0368
1	0.0039	-0.0187
2	-0.0252	0.0063

$[111]$ direction. Three types of local structure are expected when structural disorder occurs: the wrong atom tends to gather other wrong atoms on the nearby sites; the wrong atom tends to gather correct atoms on the nearby sites; the wrong atom does not affect the surroundings. It is clear that the present work supports the first. Indeed, from the considerations developed here the signs of A_1 and B_1 also support the first type between the sites of the first neighbors, although the correlation is much smaller than that for $n = 0$. Fig. 3 illustrates the situation described here.

The trend revealed by the present study can be expressed in a different way: the wrong atom is likely to form a cluster consisting of several wrong atoms along the $\langle 111 \rangle$ directions. This result and the periodic feature of the structural disorder deduced from the position of the broad peaks in Fig. 2 leads to the idea that the clusters of wrong atoms tend to be distributed periodically along the $\langle 111 \rangle$ directions. If such a periodic tendency is realized, it would reduce the collision rate between the disordered atoms and conduction electrons. Therefore, a structural disorder of this type would not affect the resistivity very much. We should not picture

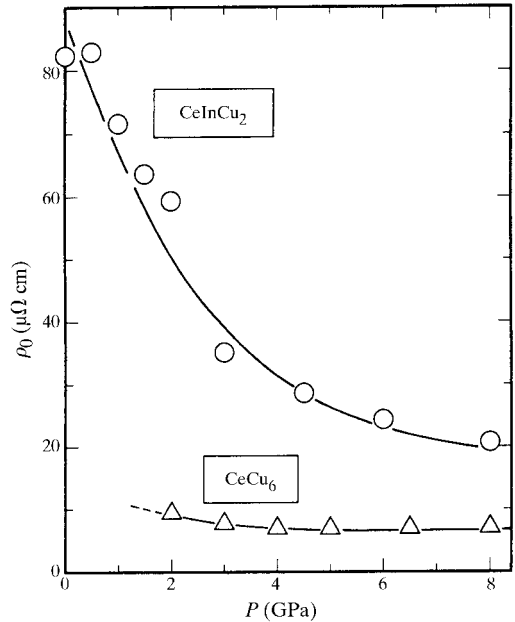


Fig. 4. Pressure dependence of residual resistivity for CeInCu_2 and CeCu_6 . The data for CeCu_6 were reported previously by Oomi *et al.* (1993).

the disorder as being the origin of the large residual resistivity of this substance. Therefore, we have to seek another mechanism for explaining the large residual resistivity, even if we find that the disorder remains at low temperature.

Finally, we mention the effect of pressure on residual resistivity ρ_0 , which may also alter our understanding of the large residual resistivity. It is well known that heavy fermion compounds form the Kondo lattice, which gives rise to a large decrease in the resistivity $\rho(T)$ at low temperature and a small $\rho(0)$ ($\equiv \rho_0$). Fig. 4 shows the pressure dependence of ρ_0 of CeInCu₂, including that of crystalline CeCu₆; the latter forms the Kondo lattice without disorder. It is clear that ρ_0 for CeInCu₂ is much larger than that of a typical heavy fermion compound at ambient pressure; this is the peculiar property of CeInCu₂ mentioned previously. However, ρ_0 shows a rapid decrease on applying pressure. Taking into account the pressure-sensitive 4*f* electron delocalization of heavy fermion compounds reported by Kagayama (1995), Andres *et al.* (1975) and Sakai *et al.* (1996), the decrease in ρ_0 could be attributed to the delocalization of the 4*f* electron of the Ce atom. We now consider that the large ρ_0 of CeInCu₂ at ambient pressure is mostly due to a disorder of the Kondo lattice and that the structural disorder of Ce and In atoms is mostly irrelevant to ρ_0 . This is quite consistent with the superstructure-like feature of the structural disorder which does not enhance the resistivity.

The authors express their sincere thanks to Professor Y. Murakami of the Photon Factory for the use of the diffractometer. One of the authors (IT) wishes to thank Dr J. Harada of Rigaku Denki Co. and Professor M. Sakata of Nagoya University who kindly encouraged this research. The Photon Factory proposal number was 93-G267. This work was partly supported by the Asahi Glass Foundation and also by a Scientific Research Grant (No. 09740252) from the Ministry of Education.

References

- Andres, K., Graebner, J. E. & Otto, H. R. (1975). *Phys. Rev. Lett.* **35**, 1779–1782.
- Kagayama, T. (1995). PhD thesis, Kumamoto University, Japan.
- Kagayama, T., Oomi, G., Takahashi, H., Mori, N., Onuki, Y. & Komatsubara, T. (1991). *Phys. Rev. B*, **44**, 7690–7693.
- Lahioe, R., Pierre, J., Siaud, E., Calera, R. M., Besnus, M. J., Kappler, J. P. & Murani, A. P. (1987). *Z. Phys. B*, **67**, 185–191.
- Onuki, Y., Yamazaki, T., Kobori, A., Omi, T., Komatsubara, T., Takayanagi, S., Kato, H. & Wada, N. (1987). *J. Phys. Soc. Jpn.*, **56**, 4251–4254.
- Oomi, G., Kagayama, T., Takahashi, H., Mori, N., Onuki, Y. & Komatsubara, T. (1993). *J. Alloys Compd.* **192**, 236–239.
- Sakai, T., Kagayama, T., Oomi, G., Sumiyama, K., Homma, Y. & Suzuki, K. (1996). *J. Phys. Soc. Jpn.*, **65**, 1154–1157.
- Takayanagi, S., Woods, S. B., Wada, N., Watanabe, T., Onuki, Y., Kobori, A., Komatsubara, T., Imai, M. & Asano, H. (1988). *J. Magn. Magn. Mater.* **76–77**, 281–282.