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Low Temperature Crystal Structures of Heavy-Fermion Compounds Ce_3Al and Ce_3Sn

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We have examined the crystal structures of heavy-fermion compounds Ce_3Al and Ce_3Sn at low temperatures by neutron diffraction. The Ce_3Al compound retains the monoclinic structure (the y-phase), with the angle between the a and *b axes* is very close to 90 °, down to the lowest temperature studied of $T = 0.35$ K. This crystal structure of Ce_3Al at low temperatures is fairly complicated, which contains sixteen atoms in the unit cell, and is originated from a small distortion from the hexagonal structure (the a-phase) found at higher temperatures. Although two structural phase transitions have already been observed in Ce_3Al, our results show that no structural phase transition is involved in the magnetic phase transition. On the other hand, the diffraction pattern taken at $T = 1.8$ K on the Ce_3Sn compound shows that it retains the fcc structure found at high temperatures. In which the Sn atoms located at the corners of the cubic unit cell and the Ce atoms at the center of each face of the cube. This crystal structure of Ce_3Sn is relatively simple, which contains only four atoms in the unit cell.

I. INTRODUCTION

Intermetallic compounds containing Ce and U have attracted considerable interest for many years, since they exhibit essentially all possible ordered states [1-5]. This class of materials is usually characterized by a specific heat at low temperatures that is two or three orders-of-magnitude larger than that of the ordinary metals. Two major physical characters can be immediately deduced [2,5] from this unusual property: Firstly, the conduction electrons may have effective masses that are two or three orders-of-magnitude larger than that of the free electrons. This class of materials is hence called heavy-fermion systems. Secondly, the bandwidth temperature of the systems is two or three orders-of-magnitude smaller than the typical Fermi temperatures found in most metals. Moreover, the heavy-fermion compounds also possess unusual superconducting and magnetic properties, where superconductivity and magnetism are no longer mutually inimical and magnetic interactions can give rise to superconductivity [4]. The unusual properties of heavy-fermion systems are nowadays believed to be originated from the strong coupling between the conduction electrons and fluctuating f-electron moments.

Both systems of Ce_3Al and Ce_3Sn belong [6] to the heavy-fermion class of materials, and show no superconductivity with a temperature down to 0.4 K. Three structural phases have been recognized [7,8] in the Ce_3Al system, while no structural phase transition has been observed so far in the Ce_3Sn system. Above 520 K, Ce_3Al crystallizes into the fcc Cu_3Au-type [9] of structure (designated the P-phase), in which the Al atoms occupied the corners of the cubic unit cell while the Ce atoms occupied the centers of each face of the cube. Below this temperature, Ce_3Al transforms into the hcp Ni_3Sn-type [9] of structure (designated the o-phase). In which the Ce atoms occupied the corners as well as the midpoints between the corners of the basal plane (the ah-plane) of the hexagonal unit cell, while the Al atom occupied the center of that basal plane. The unit cell contains two layers of atoms, and the second layer may be obtained by translating the basal layer by 1/6, 1/3, and 1/2 of the unit lattices along the a, b, and c axes, respectively. It has also been found [6] that Ce_3Al undergoes another phase transition to a heavy-fermion ground state at $T = 115$ K, in which the f-electron moments are strongly coupled to the conduction electrons and to one another. Originally, it was believed [10] that the heavy-fermion phase has the same crystal structure as that of the hexagonal a-phase found at higher temperatures. More recently, neutron diffraction measurements [8] made at $T = 15$ K show that the crystal structure of the heavy-fermion phase is in fact monoclinic (designated the y-phase) rather than hexagonal.

The temperature of 15 K is much higher than the observed [6,11] antiferromagnetic ordering temperature of $T_N = 2.5$ K for the Ce spins. In this paper, we report the low-temperature crystal structure of Ce_3Al studied by neutron diffraction. We have taken the Ce_3Al compound to a temperature as low as 0.35 K, and find a monoclinic crystal structure, which is the same structure as the reported [8] y-phase. And there is no structural phase transition is involved in the magnetic phase transition. In addition, we have also studied the low-temperature crystal structure of Ce_3Sn. It has been found [12,13] that Ce_3Sn crystallizes into the fcc Cu_3Au-type of structure at high temperatures. Our studies show that it retains the same fcc structure down to $T = 1.8$ K (the lowest temperature studied), and *no* magnetic phase transition was observed either.

II. EXPERIMENTAL DETAILS

All samples were prepared by the arc-melting technique in a helium atmosphere.

Ingot samples of ~ 10 g were prepared for both compounds, and the arc-melting process was repeated for at least 20 times to assure homogeneity. After arc melting, all samples were sealed under vacuum in preventing from oxidation. Each compound was then subjected to an appropriate annealing treatment: The ingots of Ce_3Sn were annealed at 500 °C for 2 weeks, followed by slowly cooled to room temperature. And the ingots of Ce_3Al were first annealed at 500 °C for 3 days and then at 200 °C for another 3 weeks to release strains and promote conversion from the cubic to the hexagonal phase. Both samples thus obtained are highly ductile, in which the Ce_3Sn may gradually oxidize into a dusty form while the Ce_3Al is quite stable against oxidation.

X-ray diffraction was used to examine and characterize the samples, and the diffraction patterns were all taken at room temperature. As expected, the Ce_3Al sample shows a hexagonal Ni_3Sn-type of structure, i.e. the a-phase. The lattice parameters that we obtained at room temperature were $a = b = 7.046(1)$ Å and $c = 5.447(3)$ A. No obvious X-ray lines that belong to the fcc Cu_3Au-type of structure, i.e. the P-phase, were revealed. We estimated that our sample consists less than **1%** of the P-phase at room temperature. It appears that our annealing process has removed, within experimental accuracy, the β-phase. The X-ray diffraction pattern taken on the Ce_3Sn sample is well described by the fcc Ce_3Au-type of structure. The lattice parameter that we obtained for Ce_3Sn at room temperature is $a = 4.942(5)$ A.

Neutron diffraction experiments were conducted using the BT-9 triple-axis spectrometer at the Research Reactor at the US National Institute of Standards and Technology (NIST). The incoming neutrons had a wavelength of 2.352 Å(14.8 meV) defined by a pyrolytic graphite PG(002) monochromator, with a PG filter placed before the monochromator to suppress the higher-order wavelength contaminations. Three collimators were used along the path of the neutron beam: one before the monochromator, one between the monochromator and the sample, and one after the sample. The angular collimations were 40'-48'-48' full width at half maximum (FWHM) acceptance. No analyzer crystal was used. The samples were mounted in cylindrical aluminum cans filled with helium exchange gas to facilitate thermal conduction at low temperatures. The Ce_3Sn sample was cooled using a pumped ^4He cryostat, and the lowest temperature obtained was 1.8 K. While a pumped ^3He cryostat was used to cool the Ce_3Al sample, and the lowest temperature obtained was 0.35 K. During the course of low temperature experiments, for each temperature change sufficient time was given for allowing the sample to reach thermal equilibrium.

III. RESULTS

To analyze the observed neutron scattering intensities we must compare them with model calculations. The integrated intensity for a nuclear Bragg reflection can be written *as* [14]

$$I_N = C\frac{M_{hkl}}{\sin(\theta)\sin(2\theta)}|F_N|^2,$$

where C is an instrumental constant, which depends on the neutron flux from the reactor, the collimations used, the counting time, and the quantity of the sample. However, it is a constant if the instrumental setup remains unchanged during the course of experiment. M_{hkl} is the multiplicity of the $\{hkl\}$ powder reflection, and 28 is the scattering angle for the reciprocal lattice vector $\vec{\tau}$. The nuclear structure factor F_N is defined as

$$F_N = \sum_{j=1}^{N} b_j \exp(-w_j)\exp(i\vec{\tau}\cdot\vec{r}_j),$$

where b_j is the coherent nuclear scattering amplitude for the j^{th} atom located at position $\vec{r}_j, w_j$ is the Debye-Waller factor which accounts for the effect of thermal vibrations of the atoms, and the sum extends over all atoms in the unit cell. A detailed comparison of the model calculation for the integrated intensities of the observed Bragg reflections can then quantitatively test the model used.

III-1. Ce_3Al

Figure 1 shows a portion of the diffraction pattern taken at T = **4** K, where eight individual peaks are clearly revealed. No reflection peaks were observed between 2θ = 5 ° and 20 °, this portion of the data is therefore not shown. The solid lines are least-squares fits to the Gaussian instrumental resolution function. Since there are two types of crystal structure that have been reported for the Ce_3Al at low temperatures [7,9]. We therefore use both reported structures, i.e. the hexagonal α-phase and the monoclinic y-phase, to fit the observed data. Firstly, three clearly observed peaks at 2θ = 22.45 °, 34.06, and 44.30 ° can not be indexed if the hexagonal structure was used. Secondly, a very strong peak at 28 = 47.65 ° and a relatively weak peak at $2\theta =$ 53.41 ° are also expected by the hexagonal a-phase. These characters contrast to the observation. Our observed diffraction pattern *can* not be described by the hexagonal structure.

On the other hand, the monoclinic y-phase fits very well to the observations. The observed and the model-calculated peak positions and integrated intensities using monoclinic structure with refined atomic positions are listed in Table I. Each observed peak shown in Fig. 1 may contains more than one reflection; the sum of the intensities of those reflections that may not be resolved in the experiment are listed under I_{sum}. It is those intensities listed under this column shall be used to compare to the observed intensities listed under I_{obs}. The indices shown in Fig. 1 are based on the monoclinic γ-phase. This low temperature phase is nearly orthorhombic, as the angle γ between the a and b axes is very close

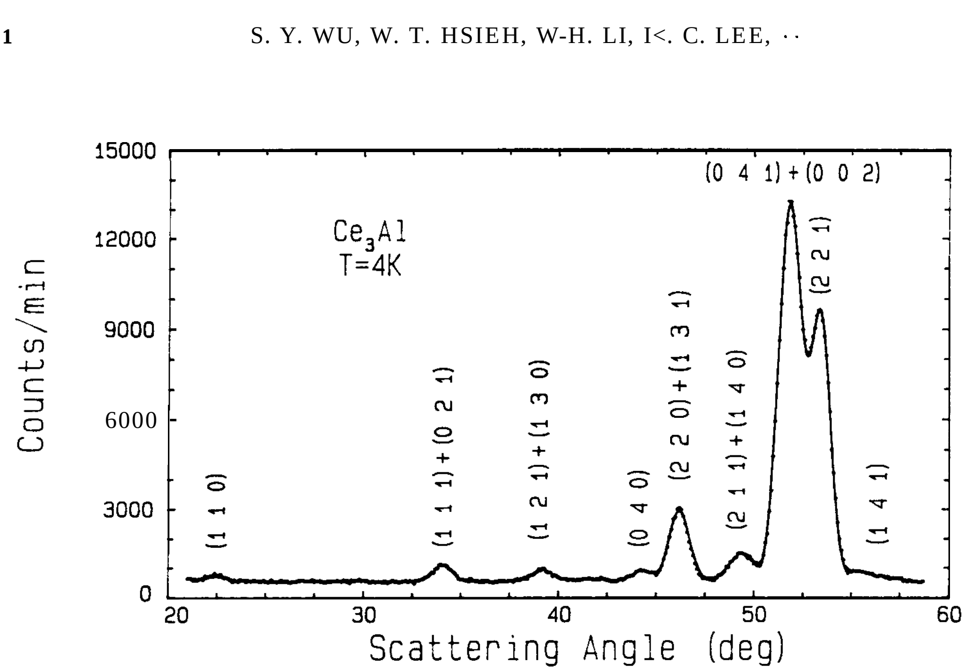

FIG. 1. A portion of the diffraction pattern observed in Ce_3Al at T = 4 I<. The indices shown are based on the monoclinic unit cell, and the solid lines are least-squares fits to the Gaussian instrumental resolution function.

to 90 °. Owing to our resolution limit, we are reluctant to perform refinement on the value for the y angle. In the model calculations we therefore adopted the value of $\gamma = 89.69$ ° reported [7] by Lawson et al.

The y-phase is fairly complicated, but is closely related to the α-phase. The crystallographic structure of the hexagonal o-phase is formed from alternating Ce-Ce chains and Ce-Al chains, and the unit cell contains six Ce atoms and two Al atoms. In the monoclinic y-phase, both the Ce-Ce chains and the Ce-Al chains are distorted, in such a way that the constitutent atoms in each chain are no longer located along a perfectly straight line and the unit cell along the b-axis doubles that of the a-phase. There are twelve Ce atoms and four Al atoms in the unit cell. As in the α-phase, the y-phase also contains two layers of atoms in the unit cell. The 2nd layer may be obtained by rotating the 1st layer through 180 ° along the axis that is perpendicular to the ab-plane and passes through the center of the unit cell, i.e. $x \rightarrow 1 - x, y \rightarrow 1 - y$, and $z \rightarrow z + 1/2$. The crystal structure of the low-temperature monoclinic γ-Ce_3Al is shown in Fig. 2, where the larger and smaller circles represent the Ce and Al atoms, respectively. And the solid and open circles represent the atoms that are located in the 1st and 2nd layers, respectively, of the unit cell. The atomic positions that we obtained for each atom in the unit cell are given in Table II.

The diffraction pattern taken at $T = 0.35$ K shows not only the nuclear Bragg peaks but also the magnetic Bragg paks. This temperature is already well below [6,11] the antiferro-

TABLE I. The observed and the model-calculated peak positions and integrated intensities for Ce_3Al at T = 4 K using a monoclinic structure (the y-phase).

			Calculated			Observed	
h	k	l	I_{cal}	$2\theta_{cal}$	I_{sum}	$2\theta_{obs}$	I_{obs}
1	1	0	1.00	22.60	1.00	22.45(3)	1.00(9)
0	2	1	0.36	33.60	2.40	34.06(1)	3.09(9)
1	1	1	2.04	34.16			
1	3	0	0.25	38.69	3.67	39.17(2)	2.34(9)
1	2	1	3.42	39.29			
0	4	0	2.49	44.39	2.49	44.30(2)	2.10(8)
2	2	0	14.66	46.14	14.75	46.18(1)	13.20(9)
1	3	1	0.09	46.78			
1	4	0	2.29	49.03	8.16	49.42(1)	7.98(7)
2	1	1	5.87	49.41			
0	4	1	47.68	51.76	77.55	51.85(1)	81.70(9)
0	0	2	29.87	51.90			
2	2	1	50.73	53.34	50.73	53.41(1)	49.72(9)

magnetic ordering temperature of the Ce spins. The magnetic ordering of the Ce spins in Ce_3Al is subjected to a separated studies [11]. Subtracting the diffraction pattern taken at T = 4 K from that taken at T = 0.35 K results in a cancellation, within experimental error, of all the nuclear Bragg peaks. The crystal structure of Ce_3Al at these two temperatures is therefore the same. We then conclude that Ce_3Al retains the monoclinic y-phase down to T = 0.35 K (the lowest temperature studied). The lattice parameters that we obtained at T = 0.35 K are $a = 6.876(2)$ Å, $b = 12.446(4)$ Å, and c = 5.341(2) Å.

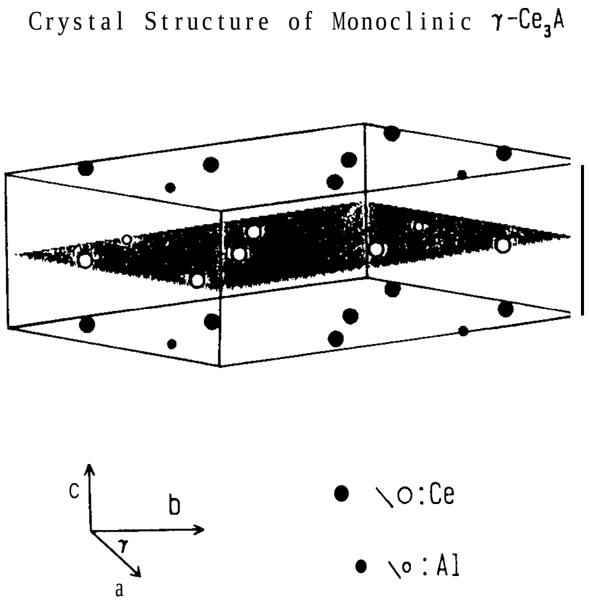

FIG. 2. The crystal structure of the monoclinic γ-Ce_3Al. The larger and smaller circles represent the Ce and Al atoms. And the solid and open circles represent the atoms that are located in the 1st and 2nd layers, respectively, of the unit cell.

111-2. Ce_3Sn

Figure 3 shows a portion of the diffraction pattern taken on Ce_3Sn at $T = 1.8$ K. No reflection peaks were observed between $2\theta = 5°$ and $20°$, this portion of the data is therefore not shown. The solid lines are least-squares fits to the Gaussian instrumental resolution function. There are only four individual peaks that are revealed in the diffraction pattern shown in Fig. 3, which indicates a relatively simple crystal structure and a highly symmetrical unit cell for Ce_3Sn. Moreover, the widths of all the observed peaks fit into the instrumental resolution, showing that each individual peak observed contains only one reflection. The observed diffraction pattern shown in Fig. 3 is well described by the fcc Cu_3Au-type of structure, and the indices shown are based on the cubic unit cell. This is the same crystal structure as that was found at high temperatures. The observed and the model-calculated peak positions and integrated intensities using fcc structure are listed in Table III, while the atomic positions of each atom in the unit cell are listed in Table IV.

The crystallographic structure of the Ce_3Sn is formed from alternating Ce-Sn planes and Ce planes, as shown in Fig. 4 where the open and solid circles represent the Ce and Sn

TABLE II. The atomic position of each atom in the unit cell of the monoclinic γ-Ce_3Al. The uncertainty for the X and Y coordinates are 0.004 and 0.003, respectively.

Atom	X	Y	Z
Ce	0.064	0.193	0
Ce	0.285	0.405	0
Ce	0.495	0.655	0
Ce	0.736	0.932	0
Ce	0.791	0.437	0
Ce	0.218	0.937	0
Al	0.950	0.690	0
Al	0.500	0.161	0
Ce	0.936	0.807	1/2
Ce	0.715	0.595	1/2
Ce	0.505	0.345	1/2
Ce	0.264	0.068	1/2
Ce	0.209	0.563	1/2
Ce	0.782	0.063	1/2
Al	0.050	0.310	1/2
Al	0.500	0.839	1/2

atoms, respectively. The cubic unit cell contains three Ce atoms and one Sn atom. The Sn atoms located at the corners of the unit cell and the Ce atoms at the center of each face of the cube. The diffraction patterns taken at $T = 30$ K, 25 K, 15 K, and 10 K all show the same crystal structure. We conclude that the Ce_3Sn retains the fcc structure down to $T = 1.8$ K (the lowest temperature studied). The structural phase transition observed in Ce_3Al does not occur in Ce_3Sn. The lattice parameter that we obtained for the cubic Ce_3Sn at $T = 1.8$ K is a = 4.929(8) A.

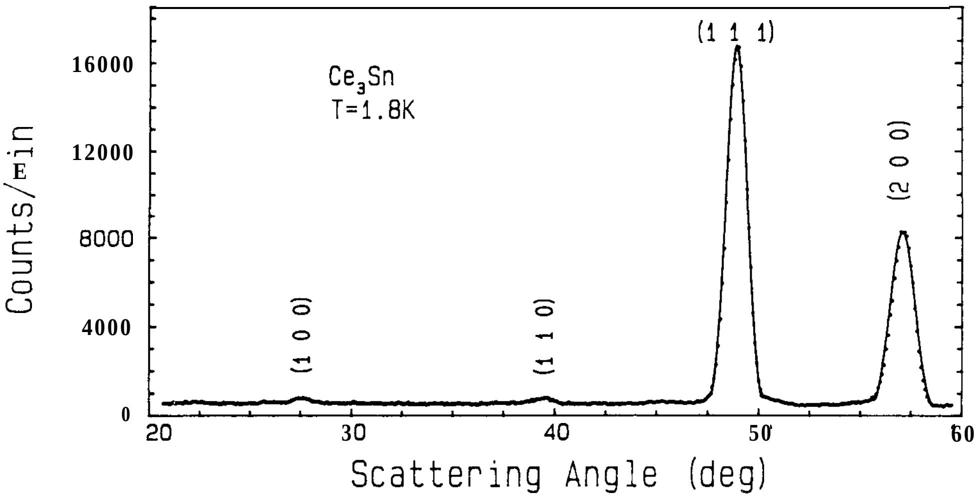

FIG. 3. A portion of the diffraction pattern observed in Ce_3Sn at $T = 1.8$ K. There are only four individual peaks that are revealed, indicating that the crystal structure is highly symmetrical. The pattern is well described by a fcc structure, and the indices shown are based on a cubic unit cell. The solid lines are least-squares fits to the Gaussian instrumental resolution function.

TABLE III. The observed and the model-calculated peak positions and integrated intensities for Ce_3Sn at $T = 1.8$ K using a fcc structure.

			Calculated		Observed	
h	k	l	$2\theta_{cal}$	I_{cal}	$2\theta_{obs}$	I_{obs}
1	0	0	27.60	0.01	27.54(3)	0.02(1)
1	1	0	39.43	0.02	39.28(3)	0.03(1)
1	1	1	48.81	1.72	48.97(2)	1.91(3)
2	0	0	57.00	1.00	57.30(2)	1.00(2)

TABLE IV. The atomic positions of each atom in the unit cell of the fcc Ce_3Sn.

Atom	X	Y	Z
Sn	0.0	0.0	0.0
Ce	0.5	0.5	0.0
Ce	0.5	0.0	0.5
Ce	0.0	0.5	0.5

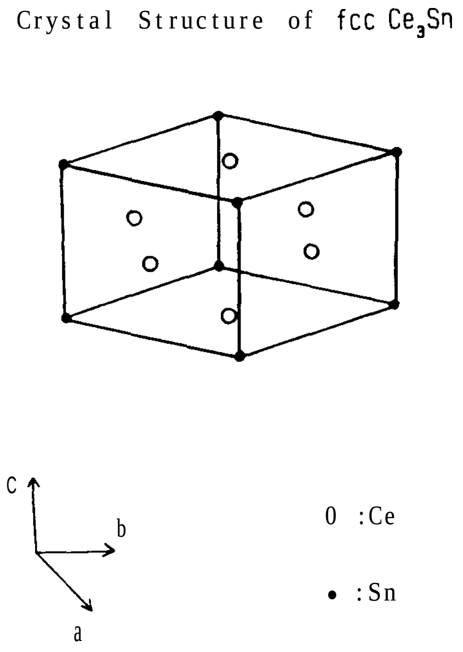

FIG. 4. The crystal structure of the fcc Ce_3Sn. The open and solid circles represent the Ce and Sn atoms, respectively.

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REFERENCES

[1] G. R. Stewart, Rev. Mod. Phys. 56, 755 (1984).

[2] P. A. Lee, T. M. Rice, J. W. Serene, L. J. Sham, and J. W. Wilkins, Comments Condensed Matter Phys. 12, 99 (1986).

[3] Z. Fisk, H. R. Ott, T. M. Rice, and J. L. Smith, Nature (London) 320, 124 (1986).

[4] Z. Fisk, D. W. Hess, C. J. Pethick, D. Pines, J. L. Smith, J. D. Thompson, and J. 0. Willis, Science 239, 33 (1988).

[5] P. Fulde, J. Keller, and G. Zwicknagl, Solid State Phys., H. Ehrenreich and D. Turnbull eds., 41, 1 (Academic Press, New York, 1988).

[6] Y. Y. Chen, J. M. Lawrence, J. D. Thompson, and J. 0. Willis, Phys. Rev. B40, 10766 (1989).

[7] K. H. J. Buschow and J. H. N. van Vucht, Z. Metallk. 57, 162 (1966).

[8] A. C. Lawson, J. M. Lawrence, J. D. Thompson, and A. Williams, Physica B163, 587 (1990).

[9] T. B. Massalski ed., Binary Alloys Phase Diagrams, (American Society for Metals, Metal Park, Ohio, 1986).

[10] T. Sakurai, T. Matsuura, and Y. Komura, J. de Phys. 49, C8, 783 (1988).

[11] W. T. Hsieh, S. Y. Wu, W-H. Li, K. C. Lee, J. W. Lynn, and Y. Y. Chen, (unpublished).

[12] S. Delfino, A. Saccone, and R. Ferro, Z. Metallkd. 71, 165 (1980).

[13] G. Borzone, A. Borsese, and R. Ferro, J. Less-Common Met. 85 195 (1982).

[14] G. E. Bacon, *Neutron Diffraction*, 3rd ed. (Clarendon, Oxford, 1975).