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Structural Phase Transition in $CeCuAl_3$ Single Crystal

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The high temperature properties of $CeCuAl_3$ single crystal were investigated by differential scanning calorimetry and high-temperature x-ray diffraction. The structural phase transition takes place around 300 °C. The phase transition changes the structural parameters only, the tetragonal $BaNiSn_3$-type structure is preserved. The significant changes of lattice parameters and especially atomic fraction coordinates with this transition are discussed with respect to the number of heating/cooling cycles and stability in time. Magnetic properties of as-cast and annealed sample are shown for comparison.

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1. Introduction

Ce-based intermetallic compounds reveal such a phenomena as valence fluctuating state, superconductivity and pressure induced superconductivity; another highly interesting phenomenon is the vibron quasi-bound state observed by inelastic neutron scattering. The vibron state was observed recently also in antiferromagnetically ordered $CeCuAl_3$ compound [1]. Although numerous studies were done, magnetic ground state of this compound remains unknown. Even the type of crystal structure was quite ambiguous many years. $CeCuAl_3$ was first reported to crystallize in the $ThCr_2Si_2$-type structure [2] with Cu and one-third of the Al atoms randomly distributed over the 4e-positions of this structure. The $BaAl_4$ structure was also mentioned in some earlier papers [3]. The powder neutron diffraction data shows the ordered $BaNiSn_3$-type structure [4]. Subsequently many further papers adopt the $BaNiSn_3$ structure [1]. On the other hand, some recent studies stated again the $BaAl_4$ structure [5]. All the previous structural studies are based on polycrystalline data. Our recent study of crystal structure on $CeCuAl_3$ single crystal reveals unambiguously the tetragonal ordered non-centrosymmetric $BaNiSn_3$-type structure [6]. Our study shows furthermore the structural phase transition around 300 °C. The investigation of this phase transition in more details as well as comparison of magnetization measurements on as-cast and annealed sample is the content of presented work.

2. Results and discussion

The preparation and characterization of $CeCuAl_3$ single crystal is thoroughly described in Ref. [6] as well as the instrumental details of the differential scanning calorimetry (DSC), high-temperature x-ray diffraction and magnetization measurements.

The electronic properties of $CeCuAl_3$ are slightly influenced by sample thermal treatment [7]. The annealing of the sample improves generally its quality. The knowledge of the phase diagram is essential for an appropriate thermal treatment. We have performed DSC measurement to reveal the melting temperature (determined as 1275 °C) [6]. Surprisingly, we have observed a further phase transition at 320 °C in the course of these measurements. The clear λ-peak corresponding to the second order phase transition was observed on DSC scans for both, heating and cooling regimes. The peaks on heating and cooling curves correspond to the endothermic and exothermic reaction, respectively. The enthalpy bounded with phase transition differs for these regimes (smaller for cooling regime), which might suggest a certain change of structure after the heating/cooling cycle [6].

The microscopic origin of this phase transition was revealed by the high-temperature powder x-ray diffraction. The temperature dependence of lattice parameters (not shown) displays a significant change from linear behaviour around 300 °C, the fraction atomic coordinates show then an abrupt jump, see Fig. 1. Similar development is observed during the cooling back to room temperature, but the structure parameters do not acquire their original values, i.e. values before heating/cooling cycle. Especially conspicuous are smaller values of structural parameters c, z_{Cu} and z_{Al} (crystallographic direction [001]), the change of parameter a is less pronounced.

Moreover, the atomic coordinates z_{Cu} and z_{Al} are lowered by each heating/cooling cycle in order to occupy the positions mirrored around the centre of unit cell (see Fig. 1, only two first cycles are shown). Nevertheless, Cu and Al atoms are still in specific positions and the centre of symmetry cannot be realized (as it is realized in $BaAl_4$- or disordered $ThCr_2Si_2$-types structures). Furthermore, one month after high-temperature x-ray diffraction measurement, we performed the powder x-ray diffraction at room temperature on previously used samples (i.e. as-cast sample and for 8 days at 900 °C annealed sample) and surprisingly we refined the structure parameters almost the same as in initial as-cast sample. Not only the effect of previous measurement but also the effect of annealing of the sample almost vanished from the point of view of structural parameters.

This time development of the annealed sample denotes time instability of the change of structural parameters after undergoing of phase transition to high temperature

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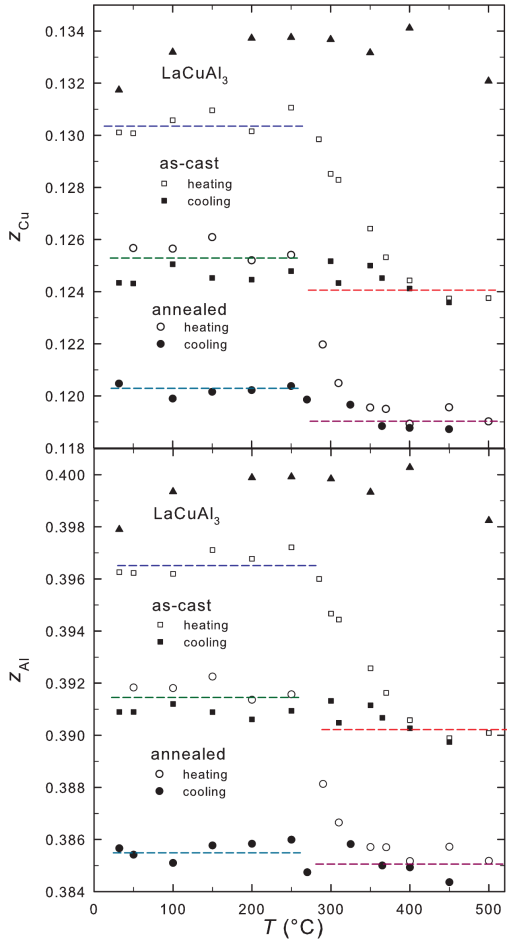

Fig. 1. The atomic fraction coordinates of as-cast and annealed $CeCuAl_3$ single crystal and $LaCuAl_3$ polycrystal. The error of determination of atomic positions is $\sim 6 \times 10^{-3}$.

phase and back. Just annealed sample structure parameters are influenced by sample history. With respect to this conclusion, we have to note that any measurement on annealed sample should be preferably done some longer time ($\sim$ one month) after the annealing process takes place to ensure structurally stable phase.

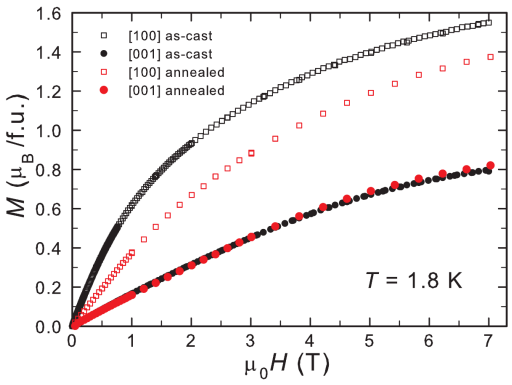

Fig. 2. The field dependence of magnetization for as-cast and annealed single crystalline samples.

The comparison of as-cast and annealed (i.e. measured more than 1 month after annealing) sample magnetization data is presented in Figs. 2 and 3. We should stress that the measurement before annealing and after annealing was performed on identical sample. Surprisingly lower magnetic moment can be observed for the annealed sample in $M(H)$ dependence for field applied in the basal plane direction ($H \parallel [100]$). The curves for $H \parallel [100]$ are almost identical in both cases. The temperature-dependence of magnetization in small magnetic fields (Fig. 3) shows only slight difference between zero-field cooled (ZFC) and field cooled (FC) regimes (only FC data are showed for better lucidity). The Néel temperature of annealed sample ($\sim$ 2.5 K) is slightly shifted to higher temperatures compared to measurement on as-cast sample ($\sim$ 2.3 K), see Fig. 3.

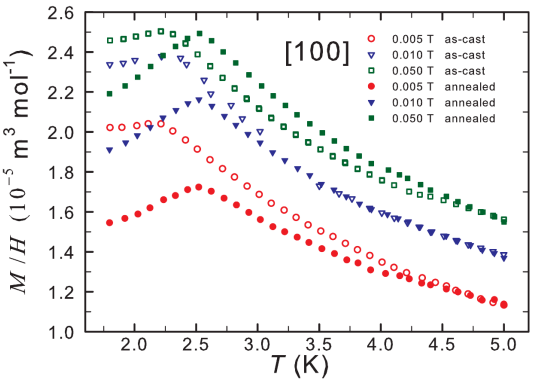

Fig. 3. The temperature dependence of magnetization in small magnetic fields under FC regime for as-cast and annealed $CeCuAl_3$ with $H \parallel [100]$ direction.

Acknowledgments

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