Experimental report

30/12/2015

Proposal: 5-31-2447 **Council:** 4/2015

Title: Temperature evolution of crystal structure and invetigation of magnetic order in Ce(Cu,Al)4 compounds

Research area: Physics

This proposal is a new proposal

Main proposer: Milan KLICPERA

Experimental team: Milan KLICPERA

Local contacts: Bachir OULADDIAF

Samples: Ce(Cu,Al)4

Instrument	Requested days	Allocated days	From	To
D20	3	2	16/10/2015	18/10/2015
D2B	0	1	26/10/2015	27/10/2015

Abstract:

Intermetallic Ce(Cu,Al)4 compounds crystallize in the ordered non-centrosymmeric tetragonal structure of BaNiSn3-type (space group 107, I4mm). Although the ground state nature of Ce(Cu,Al)4 has not been reported so far, other interesting features were found in these compounds. The highly interesting phenomenon was observed in CeCuAl3: the existence of new quasi-bound states, vibrons, arising from strong magneto-elastic coupling (CF exciton-phonon interaction) and observed as an additional peak in the inelastic neutron scattering energy spectra. Ce(Cu,Al)4 belong to materials studied within our broader project focused on existence of vibron states and its influence on magnetic and structural properties and vice versa. All compounds from Ce(Cu,Al)4 series order magnetically below 2.5 - 3 K. No other phase transition was observed down to 0.4 K. The aim of proposed experiment is to determine the magnetic structure and to map the temperature development of crystal structure in these compounds in order to observe possible distortion and/or lowering of local symmetry. Such changes of crystal structure could strongly influence the CF exciton-phonon phenomena in Ce(Cu,Al)4.

Experimental report

Experimental title: **Temperature evolution of crystal structure and investigation of magnetic order in Ce(Cu,Al)4 compounds**

Proposal number: **5-31-2447**

Instruments: **D20 + D2B**

Date of experiment: 16. – 18.10. 2015 + 26. – 27.10. 2015

Local contact: Bachir Ouladdiaf

Experimental team: Milan Klicpera[1,2], Martin Boehm[2], Pavel Javorský[1]

Affiliation: [1]Charles University in Prague, Department of Condensed Matter Physics, Ke Karlovu 5, 121 16 Prague 2, Czech Republic.

[2]Institut Laue-Langevin, 71 avenue des Martyrs - CS 20156, 38042 Grenoble Cedex 9, France.

Abstract: Intermetallic $Ce(Cu,Al)_4$ compounds crystallize in the ordered non-centrosymmeric tetragonal structure of $BaNiSn_3$-type (space group 107, *I4mm*). Although the ground state nature of $Ce(Cu,Al)_4$ has not been reported so far, other interesting features were found in these compounds. The highly interesting phenomenon was observed in $CeCuAl_3$: the existence of new quasi-bound states, vibrons, arising from strong magneto-elastic coupling (CF exciton-phonon interaction) and observed as an additional peak in the inelastic neutron scattering energy spectra. $Ce(Cu,Al)_4$ belong to materials studied within our broader project focused on existence of vibron states and its influence on magnetic and structural properties and vice versa. All compounds from $Ce(Cu,Al)_4$ series order magnetically below 2.5 – 3 K. No other phase transition was observed down to 0.4 K. The aim of proposed experiment is to determine the magnetic structure and to map the temperature development of crystal structure in these compounds in order to observe possible distortion and/or lowering of local symmetry. Such changes of crystal structure could strongly influence the CF exciton-phonon phenomena in $Ce(Cu,Al)_4$.

Scientific background:

The electronic properties of the $CeCuAl_3$ and $Ce(Cu,Al)_4$ compounds were investigated by ours previous studies. The magnetic behavior in these compounds is generally discussed as a result of the interplay between the magnetic RKKY and Kondo interactions. The magnetic properties are additionally influenced by a relatively small CEF splitting between the ground state and first excited state, which amounts to ~15 K, as found for $CeCuAl_3$ by neutron scattering experiment. Very recent inelastic neutron studies done by our group have shown that the magnetic properties are very sensitive upon Cu-Al substitution, showing considerable changes in the low energetic magnetic fluctuations as well in the CEF levels.

$CeCu_xAl_{4-x}$ compounds belong to a relatively large group of RTX_3 compounds crystallizing in the tetragonal $BaNiSn_3$-type structure (space group I4mm, 107), a non centro-symmetric derivate of the $BaAl_4$-type structure. While the electronic properties of $CeCuAl_3$ change by substituting Cu with Al atoms, the crystal structure is preserved in the whole homogeneity range between $x = 0.7$ and $x = 1.1$. Previous magnetization measurements of $CeCu_xAl_{4-x}$ crystals with $x = 0.7$, 0.8, 0.9, 1.0 and 1.1 revealed the *a*-axis as the easy magnetization axis for all concentrations and a clear strengthening of the ferromagnetic interactions with decreasing Cu content. The ordering temperature showed only weak concentration dependence (T_{ord} = 2.5 - 3 K). Although no other phase transition was observed down to 0.4 K, our previous CEF measurements show strong variations of the CEF levels with Cu doping, suggesting variations of the local symmetry around the Ce atoms. Especially, the lowest lying Γ_7 duplet seems to be strongly affected by the substitution and - suspected - distortion, thus, lowering of the local symmetry (the covalent radii of Cu and Al are 134 pm and 121 pm, respectively). Similar to the cubic $CeAl_2$ compound, this CEF level seems to interfere strongly with the low lying magnetic fluctuations and might have an influence on the long-range magnetic properties of these compounds.

Although numerous macroscopic studies on $CeCu_xAl_{4-x}$ compounds were done, details of the magnetic structure are not reported in literature so far. Our recent measurements on the stoichiometric $x = 1$ compound on D10 diffractometer show a sinusoidal spin density modulation in the tetragonal plane with propagation vector (0.4, 0.6, 0). However, the influence of the Cu doping on the magnetic structure has not been studied, yet.

Aim of the experiment:

In order to better understand the underlying crystalline mechanisms on the magnetic properties in this family of compounds, we want to complement our inelastic studies with diffraction experiments. To investigate the magnetic order (structure) in $CeCu_xAl_{4-x}$, with $x = 0.75$, 0.9, 1.0 and 1.1, and to thoroughly re-examine the temperature and x dependence of the crystal structure.

Results:

$CeCu_xAl_{4-x}$ compounds were investigated by powder neutron diffraction employing D20 and D2B diffractometers. The diffraction patterns were taken at several temperatures – typical step of 10-20 K and 2 hours statistics.

The comparison of diffraction patterns measured in ordered and paramagnetic state clearly revealed one magnetic peak at around 2θ = 14-15 degrees in all the compounds. To determine the magnetic structure from only one magnetic reflection is not possible. Nevertheless, we have refined the magnetic structure for parent $CeCuAl_3$ from single crystal data: the amplitude modulated magnetic structure is described by propagation vector (0.4, 0.6, 0), while the magnetic moments are aligned within the tetragonal basal plane along [110] direction. Using the same model magnetic structure, all Cu-Al concentrations diffraction patterns were roughly refined leading to the magnetic propagation vectors close to (0.4, 0.6, 0). In $CeCu_{0.75}Al_{3.25}$, the ferromagnetic component of magnetic moment was observed in addition.

The diffraction patterns measured in paramagnetic state were refined to obtain temperature development of structure parameters. The tetragonal crystal structure of $BaNiSn_3$–type is preserved in all the $CeCu_xAl_{4-x}$ compounds and temperatures from 1.7 to 300 K. Also, the positions of Cu and Al atoms are constant within an error of measurement (the position of Ce atoms was fixed) within each Cu-Al concentration. However, the concentration evolution of the Cu and Al atomic positions in investigated compounds reveals clear maximum at around $x = 0.95$, see Fig.1. Such a concentration dependence illustrates the influence of Cu-Al doping, i.e. filling of Cu/Al atomic positions by Al/Cu atoms, which leads to the changes of interatomic distances and therefore also electronic properties in the compound with Cu-Al substitution. Nevertheless, all structure parameters of parent $CeCuAl_3$ and $CeCu_{0.9}Al_{1.1}$ are very similar, even though the vibron states are observed only in the parent compound.
The lattice parameters *a* and *c* and therefore also *c/a* ratio and volume *V* decrease almost linearly with increasing Al content in agreement with our previous x-ray diffraction study.
The temperature development of lattice parameters is almost the same in all the concentrations, see Fig.2 as an example. The lattice parameters decrease with decreasing temperature in the temperature range 300 – 60 K and remain almost constant down to lowest-temperatures. *c/a* ratio decreases with increasing temperature, while *V* increases. The temperature dependences do not change significantly with Cu-Al concentration.

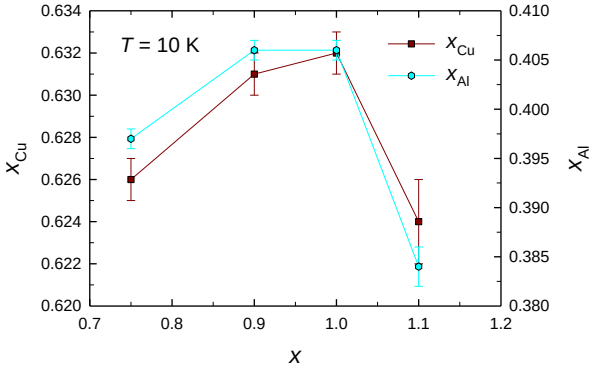

Fig.1 – The concentration evolution of atomic positions of Cu and Al in $CeCu_xAl_{4-x}$.

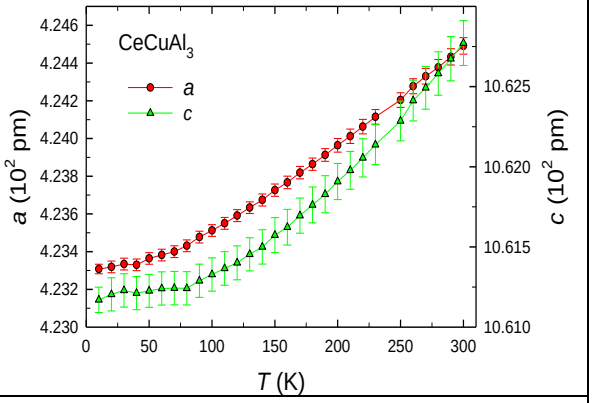

Fig.2 – Temperature evolution of lattice parameters in parent $CeCuAl_3$.