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Magnetic and structural properties of the $CeCo_{1-x}Cu_xAl_4$ (x = 0, 0.05, 0.1) compounds

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We report on the neutron diffraction, magnetic susceptibility, specific heat and electrical resistivity studies of the antiferromagnetic $CeCo_{1-x}Cu_xAl_4$ (x = 0, 0.05, 0.1) compounds. The substitution of the Co atoms by Cu aims to highlight the influence of the impurity phases on the structure stability and on the magnetic properties. For x = 0.1, 0.05 and 0 the magnetic moments of 0.76, 0.74 and 0.69 μ_B/Ce have been obtained, respectively. The phase transitions observed in the specific heat measurements suggest a presence of a small contribution of the $CeCuAl_3$ and $CeAl_2$ phases. The addition of Cu develops a small amount of the former phase and decreases strongly the amount of any other impurities stabilizing, therefore, the main $CeCoAl_4$ phase. The neutron diffraction below the Néel temperature of 13.5 K confirms most of the previous studies on the magnetic structure of $CeCoAl_4$.

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1. Introduction

The $CeCoAl_4$ compound poses a fascinating topic for in-depth studies due to its magnetic properties, which are governed solely by the Ce atoms. Co atoms are non-magnetic in $CeCoAl_4$; however, in the case of the isostructural $PrCoAl_4$ compound [1] additional magnetic transitions ascribed to a spin density wave involving the Co 3d electrons have been observed by the Muon Spin Rotation and Relaxation technique.

$CeCoAl_4$ is characterized by antiferromagnetic (AFM) order below T_N = 13.5 K and a metamagnetic-like transition in the magnetic field of about 7.5 T [2-6]. The crystallographic structure is of the $LaCoAl_4$-type (space group Pmma) with $PrCoAl_4$ being the other known example of this structure type.

Previous studies on the single crystal of $CeCoAl_4$ showed strong anisotropic properties and the lack of full saturation in magnetic fields as large as 20 T [3]. The measurements of the specific heat for magnetic fields applied along various crystal axes revealed that the Néel temperature is affected by the magnetic field in a strongly different way [2].

Dhar *et al.* [5] suggested an incommensurate antiferromagnetic order for $CeCoAl_4$ based on magnetic susceptibility, electrical resistivity and specific heat measurements. Later neutron diffraction experiments [6] have rather pointed to a collinear antiferromagnetism with a propagation vector **q** = (0, 0.5, 0.5) and a small number of unidentified reflections. The refined magnetic moment was equal to 1.29 μ_B/Ce atom. In other studies Koterlin *et al.* [7] postulated that $CeCoAl_4$ represents a magnetic Kondo lattice. This suggestion has been based on the analysis of the magnetic contribution to resistivity and on the magnetic susceptibility measurements.

The type of the propagation vector seems to be sensitive to the sample quality and its composition. In the case of the single crystal $PrCoAl_4$ a sine wave longitudinal amplitude modulated AFM structure has been observed with the incommensurate propagation vector **q** = (0, 0, 0.4087) [8,9].

To provide a new evidence within this field of investigations, we present in this paper our studies of the magnetic susceptibility and neutron diffraction on the polycrystalline $CeCoAl_4$ compound. We also address the problem of the impurity phases in this compound by verifying the effect of a small admixture of Cu at the cost of Co.

2. Experimental

The polycrystalline $CeCo_{1-x}Cu_xAl_4$ (x = 0, 0.05, 0.1) compounds were synthesized by the induction melting under an argon atmosphere. As the ingot stoichiometric amounts of the constituent elements were used.

Measurements of the magnetic susceptibility and the magnetic field dependence of the magnetization were carried out in the magnetic field up to 9 T and the temperatures down to 2 K.

Heat capacity measurements were carried out on the PPMS commercial device (Quantum Design) in the temperature range 1.9-300 K, by the relaxation method using the two-τ model.

For the electrical measurements a standard four-probe technique on a rectangular-shaped samples was used.

Neutron powder diffraction experiments were performed at the E6 diffractometer of the Helmholtz-Zentrum, Berlin. The neutron wavelength was equal to 2.43 Å. The sample was mounted in a cryomagnet with vertical magnetic fields up to 5 T. Data analysis was carried out by full-pattern Rietveld refinements using the program FULLPROF.

3. Magnetic, transport and heat capacity results

The $CeCoAl_4$ compound crystallizes in the orthorhombic $LaCoAl_4$-type structure, space group *Pmma*. X-ray diffraction shows a dominance of this structure for all the studied $CeCo_{1-x}Cu_xAl_4$ (x = 0, 0.05, 0.1) compounds. Traces of minor contributions of impurity phases have been also visible. These contributions will be discussed in next section.

In Figs. 1-3 the temperature dependence of the magnetic susceptibility is displayed for x = 0, 0.05 and 0.1, respectively. A peak resulting from the transition from the paramagnetic to the antiferromagnetic state is well visible in the figures. Within the experimental errors the Néel temperature is insensitive to the Cu contribution and T_N = 13.5 K. Our specific heat measurements provide shift of no more than 0.5 K. It implies that Cu does probably not built into the crystallographic positions. It is also supported by a rather small change of the lattice parameters with the increase of x. A different behavior has been found by Dhar *et al.* [5]. Based on the magnetic susceptibility measurements they obtained T_N reduced by 2 K for x =0.1 compared to x = 0.

Inset of Fig. 1 shows the magnetization curves for $CeCoAl_4$ at 4.2 K, 10 K and 20 K. At 4.2 K a metamagnetic-like transition occurs at field of about 7 T. This transition smears out and shifts to H = 5.7 T for T = 10 K and finally collapses to the typical paramagnetic behavior at 20 K.

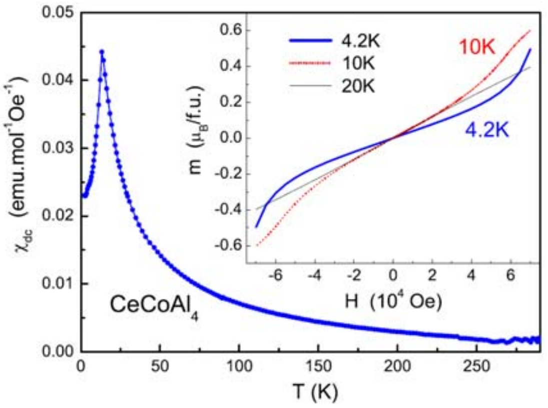

Fig. 1. Magnetic susceptibility of $CeCoAl_4$. Inset: magnetization curves at different temperatures.

The $\chi(T)$ dependence shown in Fig. 2 and Fig. 3 differs significantly from the case of x = 0 (Fig. 1), viz, a strong increase of the susceptibility occurs below T_N. It growths with the increase of the Cu content; therefore, it suggests that the contribution is caused by a creation of a Cu-based impurity phase.

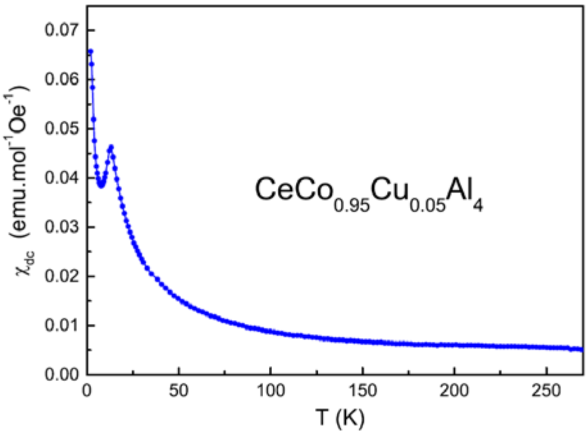

Fig. 2. Magnetic susceptibility of $CeCo_{0.95}Cu_{0.05}Al_4$.

Inset of Fig. 3 shows the magnetization curves for $CeCo_{0.9}Cu_{0.1}Al_4$ at 2 K, 5 K and 13 K. The metamagnetic-like transition occurs at a similar magnetic field as for x = 0 but is smeared out, probably due to the contribution of the Cu-based impurity phase. Besides, Fig. 3 provides an example that there is no irreversibility between the field-cooled (FC, H = 1 kOe) and zero field cooled (ZFC) curves for the studied $CeCo_{1-x}Cu_xAl_4$ compounds.

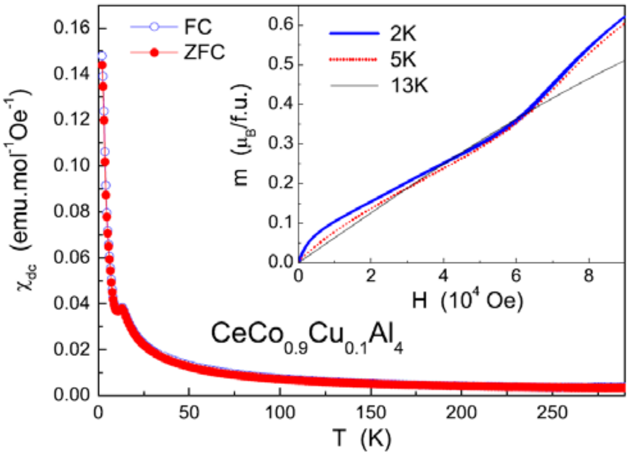

Fig. 3. Magnetic susceptibility of $CeCo_{0.9}Cu_{0.1}Al_4$ showing the lack of difference between the ZFC and FC (H = 1 kOe) mode. Inset: magnetization curves at different temperatures.

The magnetic ordering temperatures can be also well identified from the electrical resistivity and specific heat measurements. Fig. 4 and Fig. 5 depict the $\rho(T)$ dependence with the peaks at T_N revealed better in the enlarged scale illustrated in the insets. A curvature in the temperature range 20-300 K has been ascribed by Koterlin *et al.* [7] to the Kondo effect. After subtraction of the phonon contribution of a non-magnetic reference sample $\rho_m(T)$ exhibited a peak with logarithmic dependence on the high temperature side. However, such a curvature can be also well explained by the Mott-type scattering of the conduction electrons into the d band near the Fermi level.

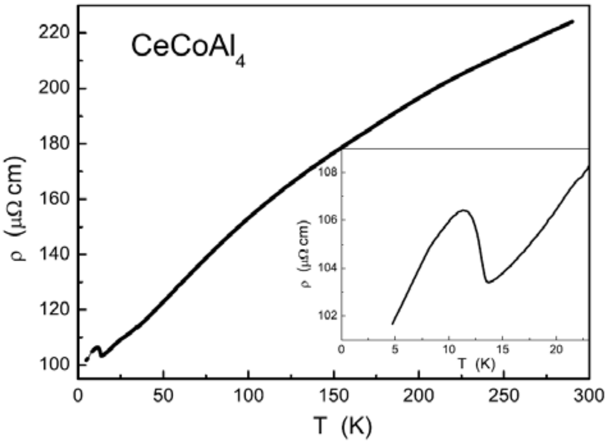

Fig. 4. Electrical resistivity of CeCoAl$_4$. Inset: the enlarged scale around the ordering temperature. Jump at about 7 K - superconductivity of the Sn electrodes.

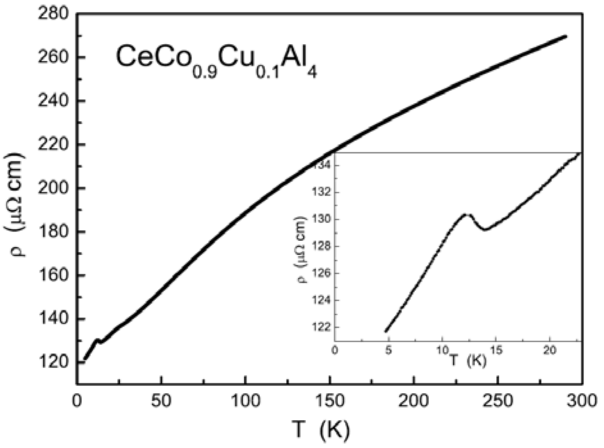

Fig. 5. Electrical resistivity of CeCo$_{0.9}$Cu$_{0.1}$Al$_4$. Inset: the enlarged scale around the ordering temperature.

The impurity phases are clearly visible in our specific heat data shown in Fig. 6 and Fig. 7. For CeCoAl$_4$ (Fig. 6) one can see an additional tiny transition at 3.9 K apart from the main peak at 13.5 K. It shifts down to about 3.8 K for the applied magnetic field of 2 T. It implies the antiferromagnetic character of this transition and we ascribe it to CeAl$_2$ as it exhibits the AFM transition in the temperature range 3.5-6 K [10,11]. For CeCo$_{0.9}$Cu$_{0.1}$Al$_4$ (Fig. 7) there are humps connected with a reduced amount of CeAl$_2$ and the additional CeCuAl$_3$ contribution.

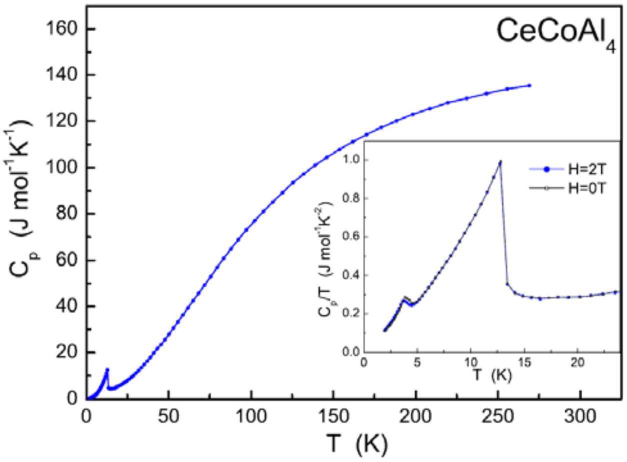

Fig. 6. Specific heat of CeCoAl$_4$. Inset: C_p/T vs. T at low temperatures.

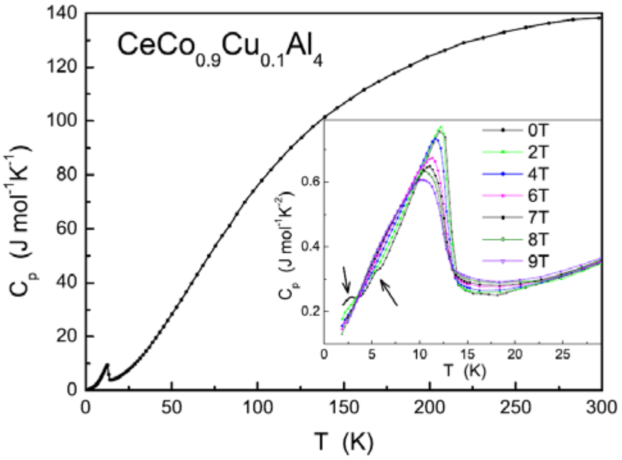

Fig. 7. Specific heat of CeCo$_{0.9}$Cu$_{0.1}$Al$_4$. Inset: C_p/T vs. T at low temperatures.

4. Neutron diffraction

We have shown in the previous section that the addition of Cu, i.e., a preparation of CeCo$_{1-x}$Cu$_x$Al$_4$ leads to a strong development of a paramagnetic contribution below T_N. Fig. 8 collects the diffraction patterns measured at 40 K for x = 0, 0.05, 0.1. For CeCoAl$_4$ apart from the main phase of the orthorhombic LaCoAl$_4$-type we observe a small amount of the CeAl$_2$ impurity (phase 'a'), which nearly disappears after the addition of Cu. Instead, with the increasing x a very small amount of CeCuAl$_3$ develops, which we suspect to be responsible for the increased magnetic susceptibility at low temperatures. CeAl$_2$ is a concentrated Kondo system with $T_K \approx 110$ K [10]; the presence of a small amount of a heavy fermion -type impurity phase could be responsible for the postulation of CeCoAl$_4$ to be a magnetic Kondo lattice [7].

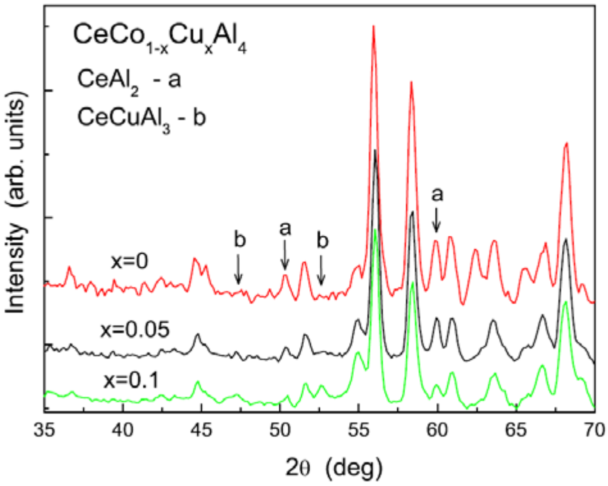

Fig. 8. The neutron diffraction pattern at 40 K for $CeCo_{1-x}Cu_xAl_4$ (x = 0, 0.05, 0.1) compounds.

From the above discussion, it is visible that the addition of Cu seems to stabilize the main phase with, probably, only a very small contribution (below 3%) of $CeAl_2$ and $CeCuAl_3$.

In Fig. 9 the neutron diffraction pattern obtained for $CeCo_{0.9}Cu_{0.1}Al_4$ at 40 K, i. e. significantly above the transition temperature, is presented together with the multi-phase refinement with the program FULLPROF. The basic parameters are compiled in Table 1. The unit cell of $CeCuAl_3$ is assumed following the studies of Moze and Buschow [12]. The strong evidence, both from the magnetic susceptibility and the neutron diffraction measurements, of the creation of the $CeCuAl_3$ impurity suggests that Cu does not built into the main phase. Moreover, the refinement indicates that the occupancy of the $CeCoAl_4$ sites is not full, which is clearly related to the creation of the minor phases.

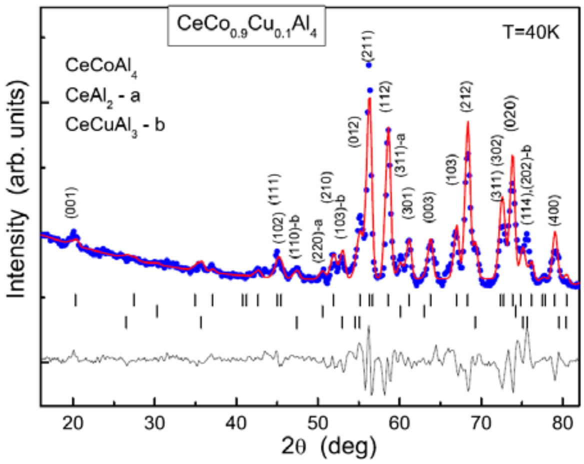

Fig. 9. The neutron diffraction pattern at 40 K refined by FULLPROF for $CeCo_{0.9}Cu_{0.1}Al_4$. The three rows of the ticks denote the structural reflections for the main and the two impurity (a, b) phases. The bottom curve corresponds to the difference between the calculated and the experimental pattern.

It should be emphasized that the presence of unidentified reflections in neutron diffraction patterns has been also mentioned in Ref. [6]. These additional contributions seem to be at least partly identified in the present paper.

Based on the structural investigations performed above the ordering temperature, the neutron diffraction measurements carried out at 2 K (Fig. 10) have been analyzed with FULLPROF, assuming additional, magnetic phase connected with the main one, i. e. $CeCoAl_4$. The magnetic contributions of the impurities has not been analyzed due to their negligible amount. One can clearly see in Fig. 10 the additional reflections, which appear at low angles and do not coincide with the structural Bragg peaks. The magnetic contribution has been refined assuming the propagation vector $\mathbf{q}$ = (0, 1/2, 1/2). The derived magnetic moment is equal to 0.76 μ_B/Ce, which is well below the saturation value for Ce^{3+} ion (gJ = 2.14 μ_B) and the value of 1.29 μ_B/Ce obtained in Ref. [6] but is in good agreement with the magnetization curves (Fig. 1 and Fig. 3).

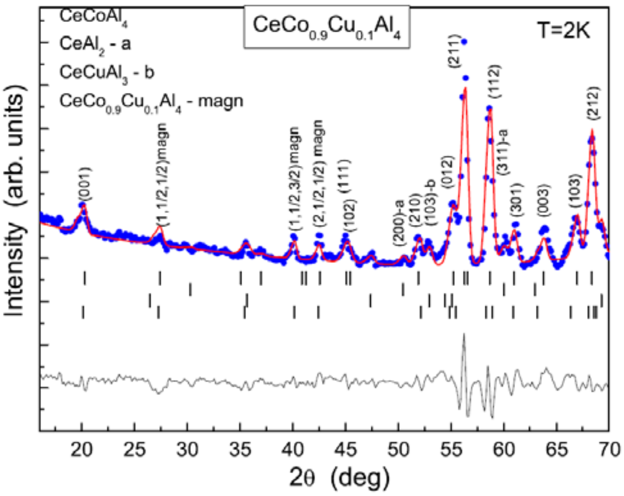

Fig. 10. The neutron diffraction pattern at 2 K refined by FULLPROF for $CeCo_{0.9}Cu_{0.1}Al_4$. The four rows of the ticks denote the structural reflections for the main and the two impurity (a, b) phases and for the magnetic phase related to the main one. The bottom curve corresponds to the difference between the calculated and the experimental pattern.

By a comparison of the intensity ratio of the magnetic and structural reflections for the three samples and knowing that for x = 0.1 μ = 0.76 μ_B/Ce, we have estimated the values of the magnetic moments for x = 0.05 and 0 as 0.74 and 0.69 μ_B/Ce, respectively.

Table 1. Atomic positions and lattice parameters of $CeCoAl_4$ (orthorhombic $LaCoAl_4$-type structure, space group Pmma).

Site	atom	x	y	z	occupancy
2e	Ce	0.25000	0.00000	0.390(3)	0.92
2e	Co	0.25000	0.00000	0.814(5)	1.00
2a	Al1	0.00000	0.00000	0.00000	1.00
2f	Al2	0.25000	0.50000	0.044(5)	0.75
4j	Al3	0.067(10)	0.50000	0.700(3)	0.88
lattice parameters					
a	7.638(5) Å				
b	4.046(2) Å				
c	6.899(5) Å				

5. Summary

We have shown that a small addition of Cu to the $CeCoAl_4$ compound stabilizes the main phase by a reduction of the amount of the impurity phases, mainly $CeAl_2$. For $CeCo_{0.9}Cu_{0.1}Al_4$ the secondary phases (about 3%) are created by $CeAl_2$ and $CeCuAl_3$.

The neutron diffraction results and the small sensitivity of the Néel temperature to the Cu addition suggest that Cu does not built into the sites of the main phase.

It seems possible that the observations of features characteristic of the Kondo system made by some authors for the $CeCoAl_4$ compound may stem from the presence of the heavy fermion impurities.

For the Cu-stabilized $CeCo_{0.9}Cu_{0.1}Al_4$ compound and below the Néel temperature $T_N = 13.5$ K we have observed an antiferromagnetic order with the propagation vector $\mathbf{q} = (0, 1/2, 1/2)$. The magnetic moment of 0.76 μ_B/Ce is reduced compared to the theoretical Ce moment and the previous results for $CeCoAl_4$.

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