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Crystal structure and magnetic properties of the off-stoichiometric compounds CeNi_3Cu_3 and CeNi_4Cu_2

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Abstract. The crystallographic properties of the compounds CeNi_3Cu_3 and CeNi_4Cu_2 have been investigated by time-of-flight neutron diffraction. A Rietveld profile refinement of the data shows that these compounds crystallize in the hexagonal TbCu_7 -type structure and that Ni atoms have a greater preference as compared with Cu atoms for occupying the $2e$ dumb-bell site. A site preference of Cu atoms for the $2c$ sites is observed. Magnetic measurements made on these compounds show that the trivalent character of the Ce atoms increases with Cu concentration.

1. Introduction

In several previous investigations we have studied the preferential site occupation in rare-earth based compounds having a crystal structure in which more than one crystallographic site is available for the non-rare-earth components [1–4]. This investigation is a continuation of previous studies which we have now extended to the TbCu_7 -type structure [5]. This structure type is a derivative of the CaCu_5 structure [6] and can be visualized as TbCu_5 in which part of the Tb sites are occupied by dumb-bell pairs of Cu atoms. In $\text{Ce}(\text{Ni}, \text{Cu})_6$ compounds this offers the possibility that the dumb-bell atoms consist of Ni pair atoms, Cu pairs or mixed pairs of atoms. Simultaneously, this also offers the possibility to have Ce atoms in this crystal structure that are coordinated differently from those in CeNi_5 and CeCu_5 , where Ce is tetravalent and trivalent, respectively. For this reason, we have also investigated the magnetic properties of these compounds. A brief account of the neutron-diffraction data has already been presented in an earlier report [7].

Intermetallic compounds derived from the CaCu_5 -type structure in which rare-earth elements are primarily combined with Ni have attracted much interest due to their application as negative-electrode materials in rechargeable Ni metal-hydride batteries [8, 9]. Research and development of metal-hydride electrodes has been focused in recent years mainly on long-term cycling stability and charge/discharge kinetics. This has led to the development of electrode materials in which not only off-stoichiometric RM_5 compounds are used but also compounds in which both the R and M components comprise at least two different

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elements. This includes mischmetal-based *R* components, which are attractive in view of cost reduction. Little is known of the atomic-scale structure of these compounds. In this study we have used neutron powder diffraction to obtain more experimental information on the structural properties of the off-stoichiometric Ce(Ni, Cu)₆ compounds.

2. Experimental methods

The compounds CeNi₃Cu₃ and CeNi₄Cu₂ were prepared by arc melting from starting materials of at least 99.9% purity. After arc melting the samples were wrapped in Ta foil, sealed into an evacuated quartz tube and annealed for two weeks at 800 K. After annealing the samples were quenched to room temperature by breaking the quartz ampoules in water. The x-ray diffraction patterns showed that the annealed samples were largely single phase, corresponding to the CaCu₅ hexagonal structure type.

Neutron powder diffraction experiments were performed at 295 K on the ROTAX high intensity powder diffractometer at the ISIS spallation neutron source [10, 11]. Data were collected in both forward and backscattering detector banks located at scattering angles of $2\theta = 37.45^\circ$ and 124.5° respectively, providing a range of accessed *d*-spacings from 0.6 to 9.0 Å.

The magnetic properties were studied on a SQUID magnetometer in the temperature range 5–350 K. For both compounds investigated we have determined the temperature dependence of the magnetic susceptibility from the slope of the magnetic isotherm measured up to 1 Tesla at various temperatures.

3. Neutron diffraction data analysis

The diffraction data collected for the compounds on the ROTAX diffractometer were analysed by the Rietveld technique [12] using the standard general structure analysis subroutine (GSAS) refinement program which least-squares refines simultaneously time-of-flight neutron powder diffraction data from several detector banks. The appropriate nuclear scattering lengths employed in the refinement ($b_{\text{Ce}} = 0.484 \times 10^{-12}$ cm, $b_{\text{Cu}} = 0.7718 \times 10^{-12}$ cm, $b_{\text{Ni}} = 1.031 \times 10^{-12}$ cm) were taken from the most up-to-date tabulations available [13]. The number of reflections contributing to the forward and backscattering detector banks were 41 and 90 respectively.

The hexagonal-type structure TbCu₇ (space group P6/mmm) was used as a trial structure, with the initial assumption of a statistical distribution of Cu and Ni atoms over the *2c*, *3g* and *2e* sites, and the additional constraint with the overall composition fixed by the nominal composition. This effectively reduces the number of occupational parameters which need to be refined by one. The origin of the unit cell was chosen at the Ce position, *1a*(0, 0, 0). Consequently, only the following parameters were refined: unit-cell constants, individual isotropic temperature factors for all sites, the *z* coordinate for the *2e* dumb-bell site and site populations of Cu and Ni atoms over the three sites, a scale factor, and peak-profile and background parameters.

Refinements made with the TbCu₇-type structure have an inherent difficulty originating from the fact that the *1a* and *2e* sites are partially occupied by Tb and Cu atoms, respectively [14]. In the refinement procedure, no restriction exists that would prevent a Tb atom from occupying a given *1a* site even though one (or both) of the two adjacent *2e* sites is occupied by Cu. In the latter case this would lead to unphysically short Tb–Cu interatomic distances. However, from energetic considerations it can be shown that such unphysical situations

Table 1. Refined crystallographic parameters for the compound CeNi₃Cu₃. Lattice constants: $a = 4.9657(1)$ Å, $c = 4.0669(1)$ Å. $R_{\text{wp}} = 4.4\%$, $R_{\text{exp}} = 3.1\%$, $\chi^2 = 2.0$.

Atom	Position	x/a	y/a	z/c	Occupancy	B (Å ²)
Ce	1a	0.0000	0.0000	0.0000	0.875	1.86(12)
Ni	2c	0.3333	0.6667	0.0000	0.460(15)	1.99(10)
Cu					0.540(15)	
Ni	3g	0.5000	0.0000	0.5000	0.513(15)	0.96(10)
Cu					0.487(15)	
Ni	2e	0.0000	0.0000	0.3035(26)	0.082(7)	1.39(10)
Cu					0.043(7)	

Table 2. Refined crystallographic parameters for the compound CeNi₄Cu₂. Lattice constants: $a = 4.9121(1)$ Å, $c = 4.0568(1)$ Å. $R_{\text{wp}} = 4.5\%$, $R_{\text{exp}} = 2.2\%$, $\chi^2 = 4.3$.

Atom	Position	x/a	y/a	z/c	Occupancy	B (Å ²)
Ce	1a	0.0000	0.0000	0.0000	0.875	1.68(12)
Ni	2c	0.3333	0.6667	0.0000	0.558(13)	1.92(10)
Cu					0.442(15)	
Ni	3g	0.5000	0.0000	0.5000	0.731(15)	1.04(10)
Cu					0.269(15)	
Ni	2e	0.0000	0.0000	0.3065(19)	0.096(7)	1.09(10)
Cu					0.029(7)	

do not occur in reality. For this reason we have interpreted the refinement results by disregarding the possibility that 1a and 2e sites are simultaneously occupied. When taking into account the different multiplicities of both sites this leads to the constraint that the sum of the occupancies of 1a and 2e sites must be equal to unity.

4. Experimental results and discussion

4.1. Crystallographic properties

The observed and calculated diffraction patterns for the compounds CeNi₃Cu₃ and CeNi₄Cu₂ are displayed in figures 1 and 2. The refined structural and thermal parameters and the corresponding R factors for CeNi₃Cu₃ and CeNi₄Cu₂ are listed in tables 1 and 2, respectively. It can be inferred from the tabulated data, that the 2c site for CeNi₃Cu₃ is preferred by Cu atoms and the 3g site is occupied on a statistical basis by both Cu and Ni atoms. For CeNi₄Cu₂, Ni atoms have a strong preference for the 3g site whilst Cu atoms preferentially occupy the 2c site. There is also a distinct preference for the Ni atoms to occupy the 2e or dumb-bell positions. A schematic diagram of the crystal structure of CeNi_{6-x}Cu_x compounds is displayed in figure 3.

The electrochemical properties of hydride-forming compounds of the type La(Ni, Cu)_x with $5.0 \leq x \leq 6.0$ and variable Ni/Cu ratios have been extensively investigated by Notten *et al* [8,9]. From a comparative study of the lattice constants derived from x-ray diffraction data, Notten *et al* concluded that for $x \geq 5$, the excess Ni/Cu atoms occupy dumb-bell positions in these compounds. They furthermore proposed that the dumb-bell atoms consist of Ni atoms only, whereas the somewhat larger Cu atoms occupy the spacious areas surrounding the dumb-bell pairs in the basal plane 2c sites. In view of

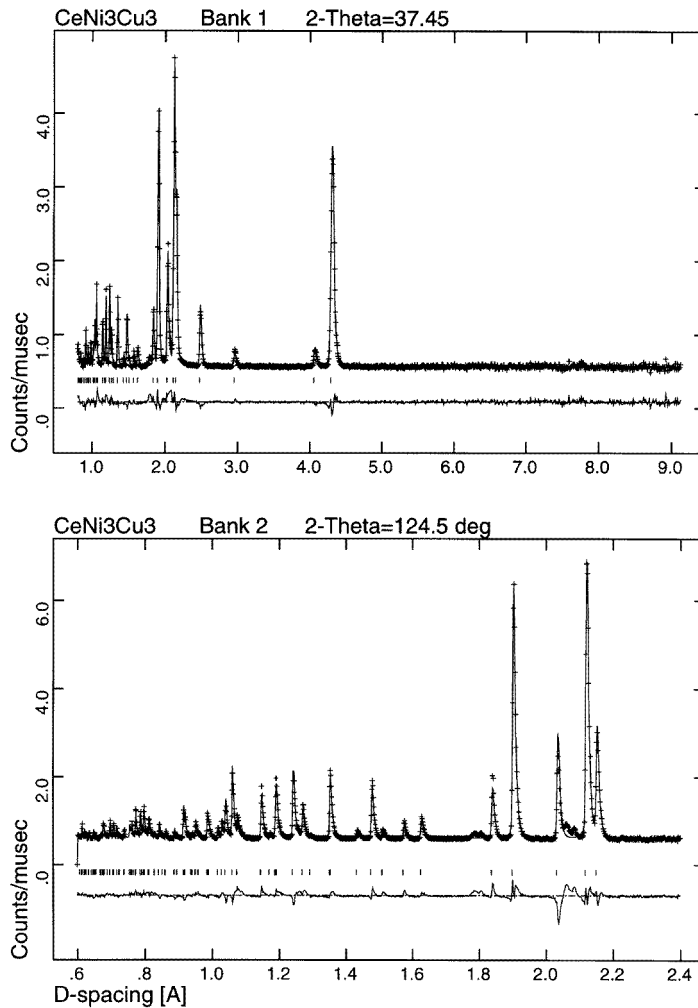


Figure 1. Observed and calculated neutron-diffraction pattern at 293 K for CeNi_3Cu_3 , displayed for both forward and backscattering detector banks.

the similarity in chemical properties and metallic radii of La and Ce, it can be expected that the preferential site occupations in the corresponding $\text{La}(\text{Ni}, \text{Cu})_x$ compounds are very similar. The results of the refinements given in tables 1 and 2 indicate a strong preference of the Ni atoms to indeed occupy the dumb-bell sites. In table 1, pertaining to CeNi_3Cu_3 of equal Ni and Cu concentrations, one finds that the Cu occupation of the $2c$ site is 17% higher than the statistical occupation of Ni and Cu atoms of this site. This tendency is even stronger in CeNi_4Cu_2 for which the results in table 2 reveal that the Cu occupation of the $2c$ site is 32% higher than the statistical occupation of Ni and Cu atoms of this site. It is also interesting to note that the $2c$ and $3g$ site occupations in these off-stoichiometric compounds are significantly different from those observed by us in the stoichiometric compound $\text{CeNi}_{2.5}\text{Cu}_{2.5}$. In the latter compound, dumb-bell pair atoms were absent, and the $2c$ and $3g$ sites were found to be statistically occupied by Cu and Ni atoms [1].

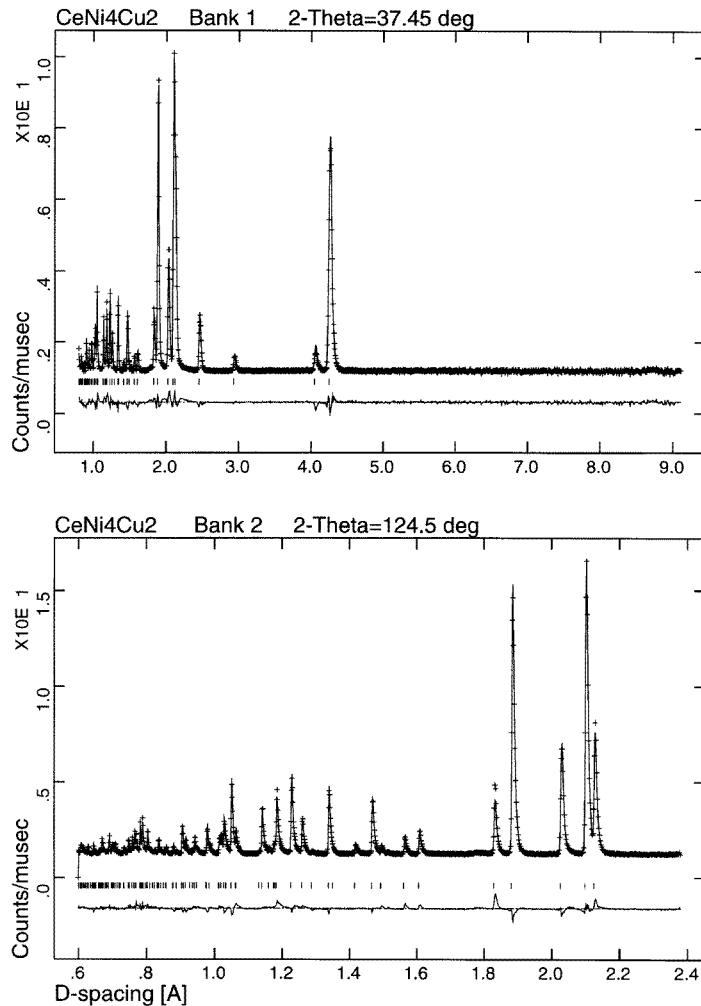


Figure 2. Observed and calculated neutron-diffraction pattern at 293 K for CeNi_4Cu_2 , displayed for both forward and backscattering detector banks.

4.2. Magnetic properties

Results of magnetic measurements made on CeNi_4Cu_2 are shown in figure 4. The magnetic susceptibility is seen to be virtually temperature independent, except for the lowest temperature range where the susceptibility rises strongly with decreasing temperature. The latter feature is frequently observed in Ce compounds and is commonly ascribed to the presence of small amounts of Ce_2O_3 . The predominantly temperature-independent character of the magnetic susceptibility shows that the Ce atoms in CeNi_4Cu_2 are close to tetravalent. The susceptibility of CeNi_4Cu_2 is roughly one order of magnitude smaller than that of CeCu_6 which is commonly regarded as an archetypal heavy-fermion system, being at the borderline between magnetic ordering and heavy-fermion behaviour [15].

The temperature-independent behaviour of the magnetic susceptibility is no longer observed in CeNi_3Cu_3 . As can be seen in figure 5, the magnetic susceptibility of this compound follows Curie-Weiss behaviour, but only approximately. The slope of the

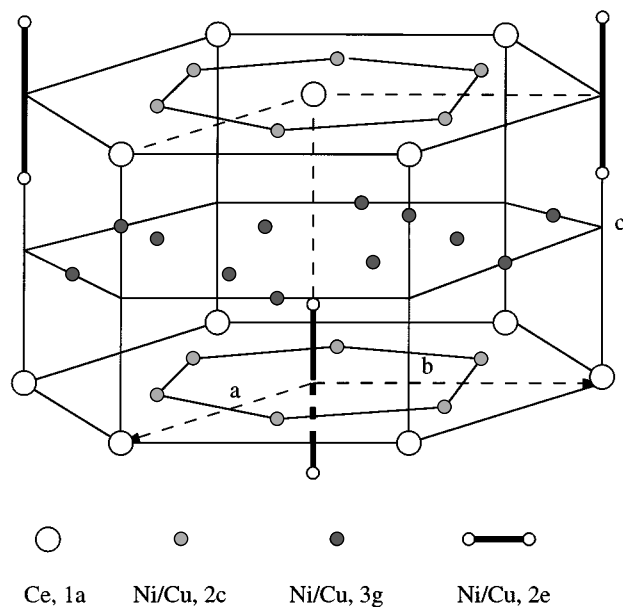


Figure 3. Hexagonal TbCu₇-type crystal structure observed for CeNi_{5+x}Cu_x compounds.

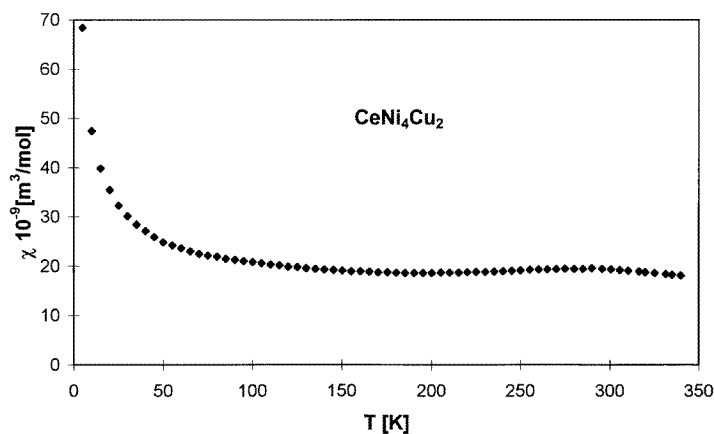


Figure 4. Temperature dependence of the magnetic susceptibility for CeNi₄Cu₂.

reciprocal susceptibility in a 100 K wide region around 100 K corresponds to $2.1\mu_B/\text{Ce}$, which is still below that expected for trivalent Ce atoms. Although the deviations from Curie–Weiss behaviour may be due to crystal field effects, there is also the possibility that only Ce atoms with relatively large numbers of Cu atoms in their coordination shell have adopted trivalent behaviour. The temperature dependence of the magnetic susceptibility of CeNi₃Cu₃ does not give any indication of magnetic ordering. The field dependence of the magnetization for CeNi₃Cu₃ shown in figure 6 suggests that if there is any magnetic ordering, it is of an antiferromagnetic type. The difference in behaviour between CeNi₄Cu₂ and CeNi₃Cu₃ in figure 6 reflects again the fact that the trivalent character of the Ce atoms has increased with Cu concentration.

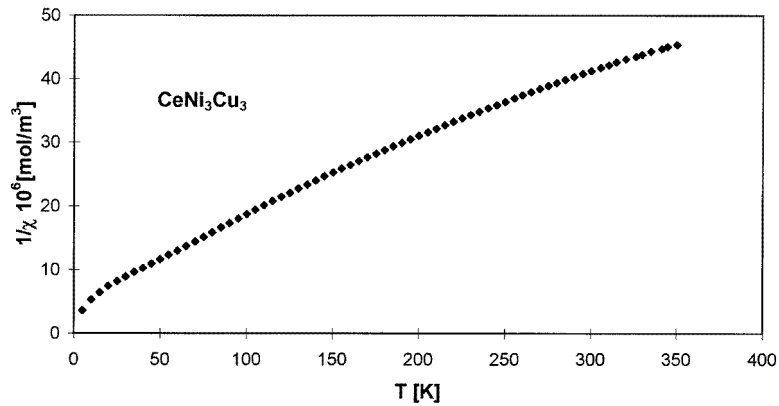


Figure 5. Temperature dependence of the reciprocal magnetic susceptibility for CeNi_3Cu_3 .

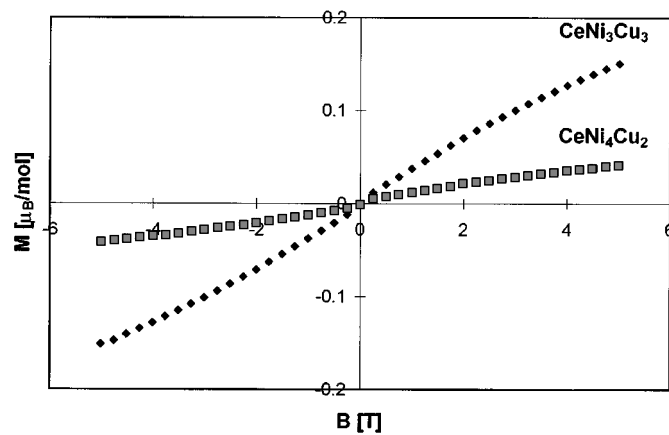


Figure 6. Field dependence of the magnetic moment of CeNi_3Cu_3 and CeNi_4Cu_2 measured at 4.2 K.

5. Conclusion

In conclusion, we have shown that the compounds CeNi_4Cu_2 and CeNi_3Cu_3 have crystallized in the TbCu_7 structure, and that the Cu and Ni atoms are not statistically distributed over the three available sites. There is a definitive preference for the Ni atoms to occupy the $2e$ dumb-bell sites. The substitution of Ni in the stoichiometric CaCu_5 -type compound CeCu_5 , where no dumb-bell atoms are present, leads to a statistical distribution of Cu and Ni over the $2c$ and $3g$ sites. In contrast, the presence of dumb-bell atoms in the compounds studied leads to a preference of the Cu atoms to occupy the $2c$ sites. We have also shown that the increasing Cu concentration in these compounds enhances the trivalent character of the Ce atoms.

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