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Magnetic and electrical properties of the tetragonal $U(Cu, Ni)_{2-x}Ga_{2+x}$ phases

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Abstract

A new family of $U(Cu, Ni)_{2-x}Ga_{2+x}$ compounds crystallizing in the $I4/mmm$ space group has been identified by means of powder X-ray diffraction analysis. The tetragonal U–Cu–Ga ternaries exist in a wide homogeneity range for $0.166 \leqslant x \leqslant 0.5$ as well as the copper-deficient $UCu_{2(1-x)}Ga_{2+x}$ phases. A tetragonal nickel derivative occurs only for $x = 1$ as $UNiGa_3$ with the $BaNiSn_3$-type symmetry ($I4mm$) or it may adopt a new type of crystal structure with the $I\bar{4}m2$ space group. All the copper ternaries were found to be antiferromagnets with a Néel temperature of around 50 K. The field dependence of magnetic susceptibility at 4.2 K indicates a non-collinear magnetic structure. The $\chi(T)$ function of $UNiGa_3$ shows a sharp maximum at 34 K and exhibits no magnetic field dependence at liquid-helium temperature. For all the ternaries examined, the electrical resistivity increases slightly with decrease in temperature and falls below the Néel temperature. The most abrupt change is observed for $UNiGa_3$.

1. Introduction

The lanthanides and light actinides form a numerous family of tetragonal compounds of $(Ln, An)T_2X_2$ stoichiometry. T here stands for a transition metal and X for an element of group IV or V, *e.g.* $X \equiv$ Si, Ge and Sn or $X \equiv$ P, As and Sb respectively. The compounds with smaller T and/or X atoms crystallize with the $ThCr_2Si_2$ structure (space group, $I4/mmm$) while those with larger atoms adopt usually the $CaBe_2Ge_2$ structure (space group, $P4/nmm$).

In the last few years there has been a great interest in studying the $LnT_2(Si, Ge)_2$ ternaries which exibit a variety of magnetic structures [1] and some of them ($CeCu_2Si_2$ and URu_2Si_2) are well known as heavy-fermion superconductors [2, 3]. Among the actinide ternaries the best known are the uranium UT_2X_2 compounds [4, 5] from which UCu_2Ge_2 and UNi_2Ge_2 are the closest analogues of the $U(Cu, Ni)_{2-x}Ga_{2+x}$ phases. UNi_2Ge_2 was found to be an antiferromagnet of AF I-type [6] while the neutron diffraction data available for UCu_2Ge_2 indicate AF II-type antiferromagnetic ordering at 4.2 K. At 43 ± 3 K it transforms into a collinear ferromagnet which vanishes at 100 ± 3 K. In both phases the moments are pointing along the tetragonal axis [6, 7].

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The effective paramagnetic moments equal to 2.40 μ_B and 3.16 μ_B are about 1.5 times larger than that in the ordered state, which are 1.61 μ_B and 2.35 μ_B for UCu_2Ge_2 and UNi_2Ge_2 respectively.

One aim of this work was to check how far the physical properties of the $U(Cu, Ni)_2X_2$ compounds are modified if one changes the p electron occupancy of the X ligand. Note that germanium has the $4p^2$ electron configuration while gallium has only one electron in the 4p shell.

On the contrary, studies on the UT_2Ga_2 systems could complete the systematic knowledge about the interaction between 5f electrons of uranium in the UT_2X_2 compounds and the $4p^1$, $4p^2$ and $4p^3$ electronic configuration of the X ligand. The importance of such an f–p interaction for understanding the magnetic properties of the rare earth and actinide intermetallics has already been proved by Takahashi and Kasuya [8–13].

2. Preparation and X-ray analysis

The samples were prepared in an arc furnace using the appropriate amounts of the elements uranium, copper, nickel and gallium of 99.99% purity. The phase analysis was performed on a DRON 1.5 powder diffractometer using Cu Kα radiation. We have started from the nominal UCu_2Ga_2 composition which gave a complex X-ray powder pattern of diffraction lines. Some of the lines were indexed as those originating from the tetragonal $ThCr_2Si_2$ body-centred structure (denoted symbolically as the θ phase). The remaining lines could be attributed to a new unknown orthorhombic phase denoted as Ω. To establish the homogeneity ranges of both the θ and the Ω phases we have prepared several $U_aCu_bGa_c$ alloys which were then checked by X-ray analysis. The results of the phase analysis are presented in Table 1. As seen from this table, in the U–Cu–Ga system except for the well-known UCuGa

TABLE 1

The results of the X-ray analysis of the U–Cu–Ga phase diagram

Nominal composition	Phases according to the X-ray pattern
UCu_2Ga_2	$\theta+\Omega$
UCu_2Ga_3	$\theta+\Omega$
UCu_3Ga_2	$\theta+\Omega$
$UCuGa_2$	θ + trace metallic U
$UGaCu_2$	Ω + trace metallic U
UCu_2Ga_4	$\Omega+UGa_3$
$U_2Cu_3Ga_5 \equiv UCu_{1.5}Ga_{2.5}$	θ
$U_3Cu_4Ga_8 \equiv UCu_{1.33}Ga_{2.66}$	θ
$U_6Cu_7Ga_{16} \equiv UCu_{1.16}Ga_{2.66}$	θ
$U_6Cu_8Ga_{15} \equiv UCu_{1.33}Ga_{2.5}$	θ
$U_3Cu_8Ga_4 \equiv UCu_{2.66}Ga_{1.33}$	Ω
$U_2Cu_5Ga_3 \equiv UCu_{2.5}Ga_{1.5}$	Ω

ternary phase there exist only two phases: θ and Ω. Furthermore, the phase analysis indicated that the tetragonal θ-type compounds have a variable composition: from $UCu_{1.33}Ga_{2.66}$ to $UCu_{1.5}Ga_{2.5}$. In addition we have also identified the copper-deficient $UCu_{1.16}Ga_{2.66}$ and $UCu_{1.33}Ga_{2.5}$ phases crystallizing in the *I*4/*mmm* space group.

The lattice parameters determined for all the tetragonal U–Cu–Ga ternaries of *I*4/*mmm* symmetry are presented in Table 2. Details concerning the orthorhombic Ω phases will be published elsewhere [14]. Considering the atomic arrangement in the $ThCr_2Si_2$ structure we suggest for $UCu_{1.5}Ga_{2.5}$ the following atom distribution: uranium (thorium) in the 2a site at 0 0 0; copper, gallium (chromium) in the 4d site at $0\ \frac{1}{2}\ \frac{1}{4}$, $\frac{1}{2}\ 0\ \frac{1}{4}$; gallium (silicon) in the 4e site at $0\ 0\ z$, $0\ 0\ \bar{z}$+body-centred translation.

Note that in $UCu_{1.5}Ga_{2.5}$, 25% of the 4d sites are occupied by the gallium atoms and 75% by the copper atoms, while in UCu_2Ge_2 all the 4d positions are filled by the copper atoms only. The atomic arrangement in the $UCu_{1.5}Ga_{2.5}$ compounds is shown in Fig. 1(a). For the substoichiometric $UCu_{1.33}Ga_{2.5}$ and $UCu_{1.16}Ga_{2.66}$ phases their atomic distribution in the *I*4/*mmm* structure

TABLE 2

Lattice parameters and interatomic distances (calculated assuming $z = 0.375$ which is approximately an average z value for all the LnT_2X_2 and AnT_2X_2 ternaries) for U–Cu–Ga ternaries crystallizing in the *I*4/*mmm* space group and $UNiGa_3$ with $I\bar{4}m2$ symmetry

Compound	Space group	*a* (Å)	*c* (Å)	U–8Cu(Ga) or U–4Ni, U–4Ga (Å)	U–8Ga (Å)
$UCu_{1.5}Ga_{2.5}$	*I*4/*mmm*	4.29	10.078	3.26	3.18
$UCu_{1.33}Ga_{2.66}$	*I*4/*mmm*	4.52	9.966	3.24	3.19
$UCu_{1.33}Ga_{2.5}$	*I*4/*mmm*	4.34	10.078	3.26	3.18
$UCu_{1.16}Ga_{2.66}$	*I*4/*mmm*	4.52	9.911	3.23	3.19
$UNiGa_3$	$I\bar{4}m2$	4.43	9.791	3.21	3.17

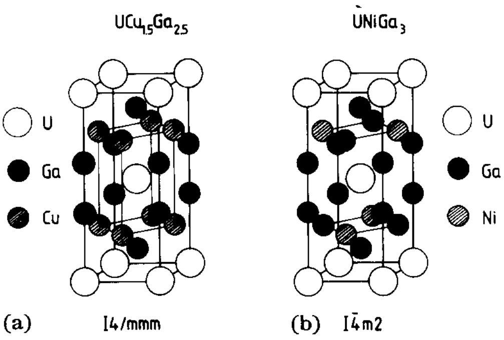


Fig. 1. Projection of crystallographic unit cell of (a) the Cu–U–Ga and (b) the Ni–U–Ga ternaries with the $BaAl_4$-type tetragonal structure.

is less evident. The vacancies may occur either in the 4d sites with the other sites 2d and 4e completely filled or they will exist only in the uranium sublattice. To distinguish between these two possibilities, neutron diffraction studies are needed.

To investigate the U–Ni–Ga system we first started to prepare $UNi_{1.5}Ga_{2.5}$ alloy. Its X-ray pattern consisted of two groups of diffraction lines, indicating the existence of both the θ and Ω-like phases in the ratio 1:1. On preparing the samples $UNiGa_3$ and UNi_2Ga_2 we obtained the X-ray single-phase patterns, indicating tetragonal and orthorhombic crystal structure for the former and latter compounds respectively.

From the powder X-ray diffraction analysis we cannot learn very much about the structure details of $UNiGa_3$. It may crystallize in the $I4/mmm$ space group with the 4e sites occupied by the gallium and the 4d sites filled randomly by 50% of the copper and gallium atoms. However, for the 1:1:3 stoichiometry there is the possibility that an ordered crystallographic structure occurs within the space group $I\bar{4}m2$, the symmetry of which is very close to that of $I4/mmm$. The atomic arrangement for $UNiGa_3$ within the $I\bar{4}m2$ space group would be the following: uranium in the 2a site at 0 0 0; nickel in the 2c site at $0\ \frac{1}{2}\ \frac{1}{4}$; gallium in the 2d site at $0\ \frac{1}{2}\ \frac{3}{4}$; two gallium atoms in the 4e site at $0\ 0\ z$, $0\ 0\ \bar{z}$ + body-centred translation.

We also cannot exclude the possibility $UNiGa_3$ possesses an ordered $BaNiSn_3$-type structure of $I4mm$ symmetry.

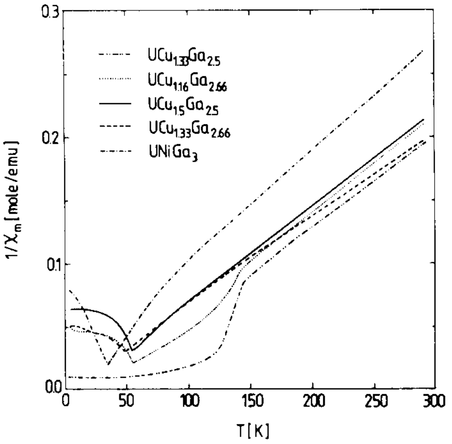
To refine the crystal structure of $UNiGa_3$ further, neutron studies are required. Data concerning an orthorhombic UNi_2Ga_2 phase will be published later [14].

3. Experimental details

The magnetic susceptibility χ was measured over the temperature range 4.2–300 K using a CAHN-RH electron balance. All changes in χ were continuously recorded with increasing temperature. The electrical resistivity $\rho(T)$ was measured over the same temperature range using a standard four-probe d.c. method. The sample voltage was measured automatically every 20 s with an accuracy of ± 1 μV. The measurements, which were repeated for the same sample and also for two different samples of a given compound, have shown full reproducibility of the results.

4. Results

The results of the magnetic susceptibility measurements performed with magnetic flux densities B of up to 0.7 T are shown in Figs. 2 and 3. As seen from Fig. 2 the temperature dependence of magnetic susceptibility strongly depends on the stoichiometry of the U–Cu–Ga ternaries. For stoichiometric $UCu_{1.5}Ga_{2.5}$ and $UCu_{1.33}Ga_{2.66}$ compounds the $\chi^{-1}(T)$ dependence



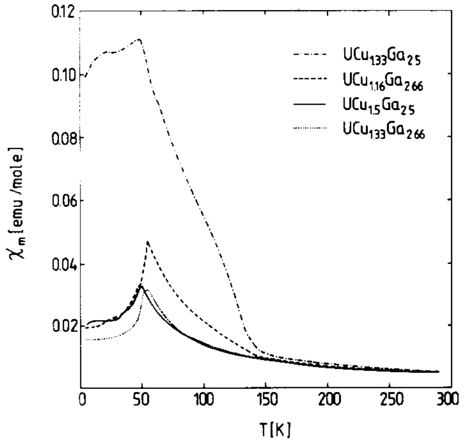


Fig. 2. Temperature dependences of magnetic susceptibility of the U–Cu–Ga ternaries obtained at $B=0.5$ T within the temperature interval 4.2–300 K.

Fig. 3. Reciprocal molar susceptibility vs. temperature for $U(Cu, Ni)_{2-x}Ga_{2+x}$ compounds showing the Curie–Weiss behaviour of $\chi^{-1}(T)$ at the relevant temperatures.

is linear within the temperature range 60–300 K. For the non-stoichiometric samples $UCu_{1.16}Ga_{2.66}$ and $UCu_{1.33}Ga_{2.5}$, $\chi^{-1}(T)$ exhibits a strong departure from the Curie–Weiss law below 150 K. This departure could be attributed either to a ferromagnetic impurity or to the intrinsic property of the non-stoichiometric samples such as, for instance, the occurrence of non-collinear incommensurate antiferromagnetism. The temperature dependence of the magnetic susceptibility for the five compounds measured here shown in Fig. 3 allows us to estimate how large the "ferromagnetic component" is. Since we have not detected in the U–Cu–Ga system any phase with a Curie point near 150 K, we believe that the "ferromagnetic component" is an intrinsic property of the non-stoichiometric compounds. The significant magnetic field dependence of the magnetic susceptibility at 4.2 K observed for all the copper-based gallides may indicate the presence of non-collinear antiferromagnetic structures at 4.2 K. In $UNiGa_3$ we have not observed a magnetic field dependence of susceptibility at 4.2 K or anomalous behaviour of $\chi^{-1}(T)$ at relevant temperatures. The magnetic data such as Θ_p and μ_{eff} derived from the linear part of the $\chi^{-1}(T)$ function are presented in Table 3.

The results of the electrical resistivity measurements for the copper-based ternaries are shown in Fig. 4. As seen from this figure the electrical resistivity slightly increases with decreasing temperature and goes through a maximum at about 120 K. Between 120 and 60 K the resistivity slowly decreases and rapidly falls below 60 K. In general, the non-stoichiometric $UCu_{1.16}Ga_{2.66}$ and $UCu_{1.33}Ga_{2.5}$ compounds exhibit a lower resistivity than do the stoichiometric compounds. The highest resistivity is observed for $UCu_{1.5}Ga_{2.5}$ which exhibits an almost semimetallic character. Electrical resistivity measurements also suggest the occurrence of antiferromagnetic ordering in the U–Cu–Ga compounds below about 50 K. It should be mentioned

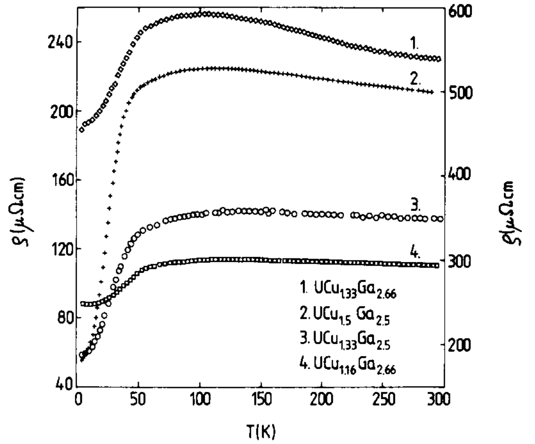


Fig. 4. Temperature dependence of the electrical resistivity within the temperature interval 4.2–300 K for U–Cu–Ga. The $\rho(T)$ behaviour may indicate the formation of a Kondo lattice in the tetragonal $BaAl_4$-type uranium ternaries.

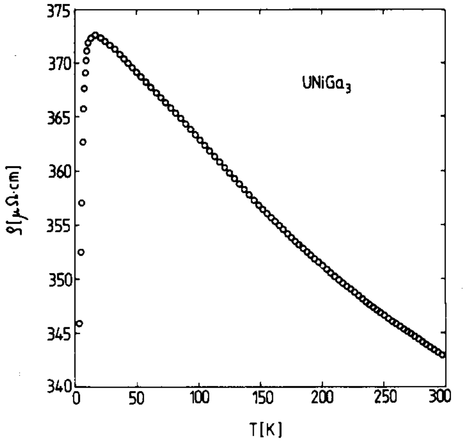


Fig. 5. The $\rho(T)$ function for $UNiGa_3$. The maximum in resistivity occurring at 37 K corresponds to the peak observed in the $\chi(T)$ function at the same temperature.

that the magnetic susceptibility anomalies appearing in the non-stoichiometric compounds at around 150 K are not associated with any significant changes in the electrical resistivity. Such a $\rho(T)$ behaviour may also support the conclusion that the anomalies in the $\chi(T)$ curve observed at 150 K are due to incommensurate antiferromagnetism which is next "locked in" below 50 K. In order to solve this problem, magnetic neutron diffraction studies are needed. In contrast with the copper-based ternaries, $UNiGa_3$ exhibits a pronounced maximum in electrical resistivity the temperature of which corresponds to the T_N in its magnetic susceptibility curve (Fig. 5). Some data obtained from the electrical resistivity measurements are presented in Table 3.

TABLE 3

Magnetic and electrical characteristics of the U–Cu(Ni)–Ga ternaries with the *I4/mmm* space group

Compound	χ_M(292 K)$\times 10^6$ (emu mol^{-1})	T_N (K)	Θ_p (K)	μ_{eff} (μ_B)	ρ(4.2 K) ($\mu\Omega$ cm^{-1})	ρ(300 K) ($\mu\Omega$ cm^{-1})	ρ_{max} ($\mu\Omega$ cm^{-1})
$UCu_{1.5}Ga_{2.5}$	5060	49	8	3.29	181.6	507	529
$UCu_{1.33}Ga_{2.66}$	4680	53	8	3.24	189.0	230	256
$UCu_{1.33}Ga_{2.5}$	5120	49	20	3.35	58.5	137	142
$UCu_{1.16}Ga_{2.66}$	4760	55	20	3.25	87.5	110	114
$UNiGa_3$	3740	37	−16	3.02	345.8	343	373

5. Discussion

Preliminary results of bulk measurements performed on the tetragonal $U(Cu, Ni)_{2-x}Ga_{2+x}$ compounds show them as an interesting group of 5f materials. The existence of the tetragonal $UCu_{2-x}Ga_{2+x}$ phases in a wide range of the copper and/or gallium concentrations may indicate that this $BaAl_4$-type derivative is thermodynamically very stable. On the contrary the respective U–ligand distances in this type of crystal structure are relatively larger than those in many binary U–Cu and U–Ga compounds, which would suggest that the appropriate chemical bondings are weaker. On these grounds, one can expect a diminishing hybridization effect which partly delocalizes the 5f level. For example, comparing the UCu_5 intermetallic with the U–Cu spacings equal to 3.05 and 2.92 Å in which the hybridization effect is rather small [15], one may expect that in $UCu_{1.5}Ga_{2.5}$ owing to larger U–ligand distances this interaction should be further weakened. On the contrary the U–Ga distance equal to 3.18 Å in $UCu_{1.5}Ga_{2.5}$ is considerably larger than that in UGa_3, being equal to 3.01 Å. This means that also the 5f–4p U–Ga interaction in $UCu_{1.5}Ga_{2.5}$ is seriously reduced in comparison with that appearing in UGa_3 which is a partly delocalized uranium system [16]. A similar situation occurs in the other ternaries examined here. Therefore we believe that the single-ion properties of the U^{4+} core in the tetragonal U–Cu(Ni)–Ga ternaries can be explained in terms of simple crystal field theory. In this work we do not intend go into the details of the crystal field calculations. They will be presented soon, when we have completed the single crystals measurements.

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