Structure and magnetism of new $R_2CuIn$ hydrides ($R = Ce, Gd$)

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Two new hydrides of intermetallic ternary indides have been synthesized – Ce$_2$Cu$_2$InH$_{2.8}$ and Gd$_2$Cu$_2$InH$_{4.5}$. Both hydrides crystallize with tetragonal structures of the Mo$_2$FeB$_2$ structure type, similar to those of the initial compounds. The relative lattice expansion reached 6.38% for Ce$_2$Cu$_2$InH$_{2.8}$ and 4.10% for Gd$_2$Cu$_2$InH$_{4.5}$. Magnetic measurements did not reveal any tendency toward magnetic ordering for Ce$_2$Cu$_2$InH$_{2.8}$ down to 5 K. In the case of Gd, hydrogenation changes the type of magnetic order from ferromagnetic for Gd$_2$Cu$_2$In ($T_C = 85.5$ K) to antiferromagnetic below 41 K for the hydride Gd$_2$Cu$_2$InH$_{4.5}$.

Hydrogen storage materials / Magnetic measurements / X-ray diffraction

Introduction

Intermetallic compounds of f-electron elements exhibit physical properties that are very sensitive to the interatomic distances and to the electronic charge distribution. In many cases hydrogenation proved to be a powerful tool for the modification of the characteristics of such compounds. For example, even slight lattice modifications can result in dramatic changes of the physical properties [1].

U$_2$T$_2$X compounds ($T$ – transition metal, $X$ – p-electron element) raised an interest as hydrogen absorbing materials mainly in the context of heavy-fermion physics [2,3]. Their properties proved to be very sensitive to the strength of the 5f–d hybridization. An interesting example is U$_2$Co$_2$Sn. In this case hydrogenation induces magnetic ordering, the type of which depends on the amount of absorbed hydrogen [2]. A slight lattice modification caused by hydrogen absorption resulted in ferromagnetic ordering, which does not occur for non-hydrogenated U$_2$T$_2$X compounds [4]. Further hydrogen absorption leads to the appearance of antiferromagnetic order similar to other magnetically ordered U$_2$T$_2$X compounds. In all known cases hydrogenation leads to the enhancement of magnetic interactions for U$_2$T$_2$X – consequently, the ordering temperatures of the obtained hydrides exceed those of the hydrogen-free U$_2$T$_2$X compounds.

The character of 5f-electron magnetism differs substantially from 4f-electron magnetism. Therefore, the investigation of the 4f-electron counterparts will provide additional information on the 2-2-1 class of compounds and will allow us to compare the impact of hydrogenation on localized versus itinerant magnetism. R$_2T_2X$ ($R$ – rare-earth metal) compounds show a remarkably large variety of magnetic phenomena [5]. The type of their magnetic ordering depends on the type of transition metal, which affects mainly the concentration of conduction electrons. Except for Ce$_2$Cu$_2$In, which is an antiferromagnet with $T_N = 5.5$ K [6], all R$_2$Cu$_2$In ($R = Gd$ - Tm) compounds order ferromagnetically [7].

The aim of our work was to study the influence of hydrogenation on the magnetism of R$_2$Cu$_2$In compounds.

Experimental details

The initial compounds Ce$_2$Cu$_2$In and Gd$_2$Cu$_2$In were synthesized by arc melting of the constituent metals under argon atmosphere and subsequent annealing in evacuated silica tubes at 870 K for 1 month.

In order to prepare hydrides, the samples were crushed into submillimeter particles and their surface
was activated by heating in dynamic vacuum (10^{-3} mbar) for 1-2 hours. After having cooled down the samples to room temperature, hydrogen gas was introduced to the system. The hydrogen pressure was 0.8 bar for Ce\textsubscript{2}Cu\textsubscript{2}In and 0.9 bar for Gd\textsubscript{2}Cu\textsubscript{2}In. Thermal cycling up to 593 K was necessary to trigger the reaction for Ce\textsubscript{2}Cu\textsubscript{2}In, while for Gd\textsubscript{2}Cu\textsubscript{2}In the reaction took place at ambient temperature. The hydrogen absorption was registered by the drop of the total pressure. Further thermal decomposition of the synthesized hydrides was performed to study the thermal stability of the samples and to determine the hydrogen content by volumetry.

The crystal structures were determined and phase analyses of the initial samples and synthesized hydrides were carried out by X-ray diffraction using Siemens D500 (Co K\textalpha) and HZG-4a (Cu K\textalpha) powder diffractometers. The crystal structure analysis was performed using a full profile Rietveld refinement.

A SQUID magnetometer was used for the magnetic studies of Ce\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} in the temperature range 5-300 K and magnetic fields up to 5 T. A Quantum Design PPMS extraction magnetometer was used for the magnetic studies of Gd\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} in the temperature range 2-300 K and magnetic fields up to 14 T. The grains of the samples were fixed in random orientation by acetone-soluble glue, which prevents rotation of individual grains under the influence of a magnetic field.

Results

After a partial survey of the R\textsubscript{2}T\textsubscript{2}In group of intermetallic compounds (R = rare-earth metal, T = Ni, Cu), it was found that hydrogenation typically leads to the decomposition of the initial compound and the formation of a rare-earth binary hydride. The only exceptions were Ce\textsubscript{2}Cu\textsubscript{2}In and Gd\textsubscript{2}Cu\textsubscript{2}In, for which the hydrides Ce\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} and Gd\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} were obtained.

The R\textsubscript{2}T\textsubscript{2}In compounds crystallize with the Mo\textsubscript{2}FeB\textsubscript{2} structure type (space group P4/mmbm, Pearson code IP10), an ordered variant of the binary U\textsubscript{3}Si\textsubscript{2} structure type. The crystal structure was confirmed by a complete structure refinement. The structure parameters agree well with literature data [8]. The synthesized samples contained a small amount of RCu\textsubscript{2}In as an impurity phase, which remained unaffected by the hydrogenation. The Mo\textsubscript{2}FeB\textsubscript{2} structure type is preserved upon hydrogenation for both Ce\textsubscript{2}Cu\textsubscript{2}In and Gd\textsubscript{2}Cu\textsubscript{2}In (Fig. 1). Hydrogenation leads to an anisotropic lattice expansion in both cases with the major contribution along the c-axis. However, while for Ce\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} expansion is observed both in the basal plane and along the c-axis, for Gd\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} a considerable expansion along the c-axis is compensated by contraction in the basal plane (see Table 1).

![Figure 1](image)

**Fig. 1** X-ray powder diffraction patterns for Gd\textsubscript{2}Cu\textsubscript{2}In (a) and Gd\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} (b) (Cu K\textalpha radiation).

Studies of the thermal stability of Gd\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} showed that hydrogen desorption takes place in two steps, namely at 625 K and 823 K. The phase analysis of the products of the decomposition showed that the crystal structure type is preserved for the intermediate hydride as well, and the initial structure is totally recovered after heating above 823 K.

| Table 1 Crystallographic data (lattice parameters a and c, unit cell volume V, relative expansion along the a direction, \(\Delta a/a\), along the c direction, \(\Delta c/c\), and the total volume expansion, \(\Delta V/V\)) for Ce\textsubscript{2}Cu\textsubscript{2}In, Gd\textsubscript{2}Cu\textsubscript{2}In and the corresponding hydrides. |
|---------------------------------|---|---|---|---|---|
| **R**\textsubscript{2}**T**\textsubscript{2}In | a, Å | \(\Delta a/a\), % | c, Å | \(\Delta c/c\), % | \(\Delta V/V\), % |
| Ce\textsubscript{2}Cu\textsubscript{2}In | 7.7334(17) | – | 3.9291(10) | – | 234.98(9) | – |
| Ce\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} | 7.8050(20) | 0.92 | 4.1040(11) | 4.45 | 250.00(11) | 6.39 |
| Gd\textsubscript{2}Cu\textsubscript{2}In | 7.5261(4) | – | 3.8137(2) | – | 216.02(2) | – |
| Gd\textsubscript{2}Cu\textsubscript{2}In\textsubscript{2.8} | 7.5075(2) | -0.25 | 3.9897(1) | 4.61 | 224.87(1) | 4.10 |
Ce$_2$CuIn is known as an antiferromagnet with $T_N = 5.5$ K [6]. Magnetic measurements for Ce$_2$CuInH$_{1.8}$ did not reveal any magnetic ordering down to 5 K (Fig. 2). The temperature dependence of the magnetic susceptibility is described by the Curie-Weiss law. Hydrogenation does not influence the effective moment, which remains $\mu_{\text{eff}} = 2.48 \mu_B$/Ce, close to the Ce$^{3+}$ theoretical value of 2.54 $\mu_B$. The value of the paramagnetic Curie temperature for Ce$_2$CuInH$_{1.8}$, $\theta_p = -14$ K, is somewhat more negative compared to $\theta_p = -7.7$ K for Ce$_2$Cu$_2$In. The field dependence of the magnetization measured at 5 K is typical for a paramagnet and can be described by the Brillouin function with a reduced value of the magnetic moment for Ce atoms ($M_{\text{Ce}} = 1.15 \mu_B$).

The difficulties to synthesize $R_2$In hydrides reflect quite general tendencies, which become apparent when comparing the hydrogenation of isotypes of rare-earth and actinide-based compounds. The rare-earth compounds often absorb hydrogen at lower pressures and/or temperatures than the actinide counterparts, but at the same time they tend to decompose, forming preferably simple binary rare-earth hydrides RH$_2$. Therefore, we could not study the whole series of $R_2$In compounds, but we had to restrict ourselves to two particular compounds, Ce$_2$CuIn and Gd$_2$CuIn, for which the synthesis of the corresponding hydrides was successful.

Ce$_2$CuIn forms a hydride with higher hydrogen content, 2.8 H/f.u., compared to 0.8 H/f.u. in the case of Gd$_2$CuIn. It agrees well with the larger relative unit cell expansion for the former intermetallic. Besides, the different character of the lattice expansion for both compounds (lattice expansion within the basal plane for Ce$_2$CuInH$_{1.8}$ versus lattice contraction for Gd$_2$CuInH$_{0.8}$) may suggest an additional hydrogen position in Ce$_2$CuInH$_{1.8}$. The stoichiometry of the rare-earth hydrides differs from the uranium counterparts, for which the amount of absorbed hydrogen is very close to 2 H atoms per formula unit for all the known hydrides, and all hydrogen is released in one step. Based on available crystallographic data we may assume that one of the most plausible positions of hydrogen in the $R_2$In–H systems is the site 8(k) located inside a $R_2$Cu tetrahedron. Occupancy of this site should affect mostly the lattice parameter c. That is exactly the case we encountered for the Ce$_2$CuInH$_{1.8}$ and Gd$_2$CuInH$_{0.8}$ hydrides.

Ce$_2$CuIn is a typical magnetic trivalent cerium compound with magnetic order. The 4f$^3$ configuration is indicated by the large volume, corresponding to the value extrapolated from the heavier rare-earths. The expansion produced by the hydrogenation can therefore not contribute to any additional 4f-electron localization. Instead, we lose the fingerprint of the magnetic order, what may indicate the change of the RKKY interaction. The Neél temperature of the initial compound is relatively low ($T_N = 5$ K) and therefore the fact that we did not observe magnetic order means...
either that it is shifted to lower temperatures or that it is totally suppressed.

The type of magnetic interactions in Gd$_2$Cu$_2$In proved to be particularly sensitive to hydrogenation. The variations of the Gd-Gd spacing and/or of the electron concentration lead to a dramatic change in the exchange RKKY interactions towards antiferromagnetic coupling. Taking into account the oscillating character of the RKKY interaction, it is understandable why a slight reduction of the Gd-Gd spacing (3.65 Å for Gd$_2$Cu$_2$InH$_{0.8}$ compared to 3.73 Å for Gd$_2$Cu$_2$In) resulted in a complete change of the character of magnetism.

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References