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Acta Cryst. (1971). B**27**, 1085

Composition and Crystal Structure of Hexagonal Cu-rich Rare Earth–Copper Compounds

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(*Received* 1 *September* 1970)

Compounds RCu_5 with the hexagonal $CaCu_5$ structure have been observed for R = La, Ce, Pr, Nd, Sm, Gd, Tb and Y. Their lattice constants are given. For R = Gd, Tb, Dy and Y a compound of the approximate composition RCu_7 has been observed. The structure and the lattice constants of these compounds are presented. The compounds RCu_7, in which R = Gd, Dy and Tb, decompose on annealing at low temperatures into RCu_5 and elementary Cu. The pycnometric density of $TbCu_7$ has been determined.

Introduction

In a previous investigation it has been shown that for the heavy rare earth elements the compounds of the form RCu_5 have the cubic $AuBe_5$ structure (Buschow, van der Goot & Birkhan, 1969). For the light rare earth elements and incidentally also for some of the heavy rare earth elements a hexagonal compound of the $CaCu_5$ type has been reported in literature (Dwight, 1961; Wernick & Geller, 1959; Haszko, 1960). The stoichiometric composition of these hexagonal phases does not seem well established, as some rare earth elements have been observed to have the $CaCu_5$ structure type in compounds of composition RCu_4 as well as in compounds of composition RCu_5 (Gschneidner, 1961). During a recent investigation of the structure of rare earth–copper compounds of the form RCu_6 indications were obtained that some rare earth–copper systems in the concentration range 80–90 at.% Cu probably have more than one hexagonal phase. To clarify this situation we have investigated this concentration range in most of the rare earth–copper systems by X-ray diffraction and metallography.

Experimental

The samples were prepared by arc melting. The purity of the starting materials was 99·99% for Cu and 99·9% for the rare earth elements. Vacuum annealing was performed in sintered Al_2O_3 crucibles sealed into quartz tubes. This procedure was found to lead to significant losses in weight of the Sm–Cu samples. Some of these samples were therefore also prepared by sealing the proper amounts of Sm and Cu under purified argon into a molybdenum container. This container was heated subsequently to a temperature sufficiently high to induce the chemical reaction. X-ray powder diffraction diagrams were obtained from both as-cast and annealed samples. After crushing in a mortar the powder was stress-relieved for 1 hour between 450 and 500 °C in a vacuum. The application of higher temperatures to compounds of the type RCu_7 invariably led to a decomposition of RCu_7 into the two adjacent phases. The X-ray diffraction data were obtained on a Philips X-ray powder diffractometer PW1050/30. Cu $K\alpha$ radiation was used together with an X-ray monochromator. The samples were metallographically examined by standard techniques.

The crystal structure of $TbCu_7$

By studying samples varying in Cu concentration from 80–90 at.% we obtained evidence for the existence of two hexagonal Cu-rich phases. The first of these was obtained by splat-cooling of a sample of composition $TbCu_5$. X-ray diffraction showed that the sample was of a single phase. The structure of this phase was easily identified as belonging to the hexagonal $CaCu_5$ structure type which had been reported before for a number of RCu_5 compounds (Dwight, 1961; Wernick & Geller, 1959; Haszko, 1960; Gschneidner, 1961). A further hexagonal phase was observed in as-cast samples of somewhat larger Cu concentrations. Samples near 87 at.% Cu were found by metallography to consist of a single phase only, pointing to a compound of the approximate composition $TbCu_7$. The corresponding X-ray diagram could be indexed according to the $CaCu_5$ structure type, although, with respect to the X-ray diagram of the splat-cooled sample $TbCu_5$ mentioned above, significant deviations of the lattice constants and the X-ray intensities were observed.

Compounds of the type AB_x with x appreciably larger than 5 and having a crystal structure closely related to the $CaCu_5$ structure, have been widely reported in the literature (Schubert, 1964). They arise from an ordered substitution in AB_5 of B elements at A sites. The complete absence of any superstructure lines in the X-ray diagram of the compound $TbCu_7$ clearly shows that this compound does not belong to this group. In order to have a compound $TbCu_7$ in which the $CaCu_5$ structure is largely conserved one is tempted to consider the following possibilities:

Case *A*. Some of the Tb sites in $TbCu_5$ are unoccupied.

Case *B*. Some of the Tb sites are occupied by one Cu atom.

Case *C*. Some of the Tb sites are occupied by a pair of Cu atoms.

Owing to the absence of superstructure lines, all these substitutions should occur at random. It is clear that in order to arrive at the 1:7 stoichiometry a decreasing amount of Tb-substitution is required in going from case *A* to *C*.

We have calculated the X-ray intensities for the three possibilities in order to compare them with the experimental data obtained for $TbCu_7$. The atomic positions used for the intensity calculations are summarized in Table 1. We also used atomic scattering factors with real dispersion corrections (*International Tables for X-ray Crystallography*, 1962). The Lorentz–polarization factor was adapted to the use of an X-ray monochromator. For the temperature factor the value $B = 1{\cdot}0$ Å^2 was used, although satisfactory results could also be obtained with values up to 20% lower. The results of the calculations and the experimental data are compared in Table 2. The rather low R value found for the structure referred to as case C seems to eliminate the other two possibilities. Additional proof was obtained from a comparison of the calculated and observed densities: The values 8·11, 8·56 and 8·85 g.cm^{-1} are the calculated X-ray densities for the structures corresponding to the cases A, B and C, respectively. Experimentally we observed the value 8·81 ± 0·02 g.cm^{-1} which, again is in favour of case C.

Table 1. *Parameters used for the calculation of the X-ray intensities of the compound* $TbCu_7$

Space group $P6/mmm$·

$(1-r)$ Tb in a: $0,0,0$
s Cu in e: $\pm(0,0,z)$
2 Cu in c: $\pm(\frac{1}{3},\frac{2}{3},0)$
3 Cu in g: $\frac{1}{2},0,\frac{1}{2};\ 0,\frac{1}{2},\frac{1}{2};\ \frac{1}{2},\frac{1}{2},\frac{1}{2}$

Case A: $r=0{\cdot}29;\ s=0$
Case B: $r=s=0{\cdot}25;\ z=0$
Case C: $r=0{\cdot}22;\ s=2r=0{\cdot}44;\ z=0{\cdot}306$

Table 2. *Calculated and observed intensities (in arbitrary units) for the compound* $TbCu_7$

Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$.

h	k	l	$\sin^2\theta_c$	I_o	$I_c(A)$	$I_c(B)$	$I_c(C)$
1	0	0	0·0324	3	15	2	0
0	0	1	0·0344	3	3	8	3
1	0	1	0·0669	77	82	105	76
1	1	0	0·0973	97	66	73	96
2	0	0	0·1298	360	83	85	105
1	1	1	0·1318		269	265	250
0	0	2	0·1378	70	86	82	76
2	0	1	0·1642	55	56	36	53
1	0	2	0·1702	7	2	0	4
2	1	0	0·2271	0	1	0	0
1	1	2	0·2351	20	31	33	25
2	1	1	0·2616	20	18	23	18
2	0	2	0·2676	37	47	48	40
3	0	0	0·2921	18	10	11	14
0	0	3	0·3101	0	0	0	0
3	0	1	0·3265	50	53	52	50
1	0	3	0·3425	5	6	7	9
2	1	2	0·3650	0	1	0	2
2	2	0	0·3894	41	40	37	44
1	1	3	0·4074	36	35	34	40
3	1	0	0·4219	0	0	0	0
2	2	1	0·4239	0	1	1	0
3	0	2	0·4299	6	10	11	8
4	0	0	0·5192	10	7	7	9
2	2	2	0·5272	37	46	43	41
2	1	3	0·5372	8	5	6	8
0	0	1	0·5512	14	7	7	7
4	0	1	0·5537		6	4	5

Table 2 (*cont.*)

h	k	l	$\sin^2\theta_c$	I_o	$I_c(A)$	$I_c(B)$	$I_c(C)$
3	1	2	0·5597	0	1	0	0
1	0	4	0·5837	0	0	0	0
3	0	3	0·6022	17	18	18	21
1	1	4	0·6486	13	5	6	6
3	2	1	0·6511	4	4	5	4
4	0	2	0·6571	13	10	10	9
$R=\Sigma\|I_o-I_c\|/\Sigma I_o$:					0·15	0·18	0·07

The structure of other RCu_7 compounds

The above structure type is also shown by the compounds $GdCu_7$, $DyCu_7$ and YCu_7. The lattice constants of these compounds and of $TbCu_7$ are given in Table 3. The compounds $GdCu_7$, $DyCu_7$ and $TbCu_7$ are not stable at room temperature. Upon annealing at 700 °C and lower temperatures a decomposition of the compounds RCu_7 into RCu_5 ($AuBe_5$ type) and elementary copper occurs in the case of $DyCu_7$ and $TbCu_7$, whereas $GdCu_7$ decomposes into $GdCu_6$ ($CeCu_6$ type) and Cu.

Table 3. *Crystallographic data for some* RCu_7 *compounds*

Compound	Lattice constants a	c	c/a
$GdCu_7$	4·951 Å	4·171 Å	0·843
$TbCu_7$	4·942	4·164	0·845
$DyCu_7$	4·932	4·156	0·844
YCu_7	4·940	4·157	0·843

These decompositions were observed both by X-ray diffraction and by metallography. The compounds $GdCu_7$, $DyCu_7$ and $TbCu_7$ are not metastable but exist only at elevated temperatures. For instance, when a sample of $TbCu_7$, which was allowed to decompose by annealing at 700 °C or lower temperatures, into cubic $TbCu_5$ and elementary Cu, is annealed subsequently at 800 °C and quenched rapidly, one obtains again a single-phase sample of the hexagonal compound $TbCu_7$. The compound YCu_7 does not decompose upon low temperatures annealing. Indications were obtained, however, that the phase stable at low temperatures occurs at slightly lower Cu concentration than corresponds to YCu_7.

The crystal structure of the compounds RCu_5

The compounds RCu_5, where R represents one of the light rare earth elements (La–Sm), were found to adopt the hexagonal $CaCu_5$ structure. The lattice constants for the latter structure type are given in Table 4. They were obtained from samples annealed for 3 weeks at 700 °C, with the exception of the compounds with R = Gd, Tb and Y which could be obtained in single-phase condition only by splat cooling. It should be stressed that the lattice constants presented in the Table refer to $CaCu_5$ type compounds of the proper stoichiometric composition. We did not observe this structure type for compounds of the formula composition RCu_4 such as cited by Gschneidner (1961) for the compounds with R = La, Ce, Nd, Gd and Y.

It was already mentioned that if R represents one of the heavy rare earth elements (Gd–Lu) the structure stable at room temperature is of the cubic $AuBe_5$ type (Buschow *et al.*, 1969).

Table 4. *Crystallographic data for some* RCu_5 *compounds*

Compound	Lattice constants a	c	c/a
$LaCu_5$	5·186 Å	4·110 Å	0·791
$CeCu_5$	5·149	4·108	0·794
$PrCu_5$	5·128	4·106	0·794
$NdCu_5$	5·110	4·104	0·790
$SmCu_5$	5·07	4·10	0·81
$GdCu_5$	5·039*	4·111	0·816
$TbCu_5$	5·030*	4·090	0·813
YCu_5	5·005*	4·097	0·812

* Splat cooled

Discussion

The lattice constants of the compounds RCu_5 presented in Table 4 for the light rare earth elements are in very good agreement with those reported by Dwight (1961), while the data reported for $GdCu_5$ and YCu_5 differ only slightly from those reported by Wernick & Geller (1959). A serious discrepancy exists, however, between our results for $TbCu_5$ and those reported by Haszko (1960). Unfortunately Haszko did not supply any information on sample preparation and annealing treatments. In view of the close resemblance of this data and those presented above for $TbCu_7$ it seems very likely that Haszko observed the phase $TbCu_7$ rather than $TbCu_5$.

A comparison of the data presented in Tables 3 and 4 shows that the c/a ratio increases significantly upon substitution of two Cu atoms at some of the R sites in RCu_5. This is in agreement with detailed investigations on similar substitutions in RCo_5 compounds (Buschow & van der Goot, 1968, 1969). There is much resemblance between the compounds of the series RCu_5 and RCo_5. In both cases the hexagonal $CaCu_5$ structure is observed only for rare earth elements in which the metallic radius is relatively large, while deviations from 1:5 stoichiometry occur for the smaller rare earth radii. For instance, instead of $ErCo_5$, a compound of composition $ErCo_6$ is observed (Buschow, 1966) in which some of the Er-sites are occupied by a pair of Co atoms (Buschow, Fast & van der Goot, 1968). In this case too, similar to those of $GdCu_7$, $TbCu_7$ and $DyCu_7$, the compound $ErCo_6$ is only stable at high temperatures and decomposes upon annealing at low temperatures into the adjacent phases. A comparison with the related Co compounds shows on the other hand that one must also consider the possibility that the stoichiometric and off-stoichiometric $CaCu_5$ type compounds have merged into one large homogeneity region which, at elevated temperatures, extends primarily towards high Co-concentrations (Buschow & van der Goot, 1968, 1969). Upon annealing at low temperatures the off-stoichiometric compound then decomposes into stoichiometric RCo_5 and R_2Co_{17}. X-ray studies on quenched samples of various compositions between RCu_5 and RCu_7 show that such a situation does not apply to the copper compounds in which $R=Gd$, Tb or Dy. This is most convincingly demonstrated for the case in which $R=Gd$, where an orthorhombic compound $GdCu_6$ is observed (Buschow & van der Goot, 1970). An annealed $GdCu_6$ sample consists entirely of the orthorhombic phase notwithstanding whether the sample was quenched after annealing or not.

We prepared in addition a sample of the formula composition $GdCu_{6\cdot5}$ and annealed it for 3 weeks at 700°C. At this temperature the phase $GdCu_7$ is still stable. After quenching of the sample from this temperature, microscopic and X-ray investigations showed the presence only of a mixture of the phases $GdCu_6$ and $GdCu_7$. The lattice constants of the phase $GdCu_7$ corresponding to this two-phase region are $a=4\cdot961$ and $c=4\cdot156$ Å. Within experimental error ($\pm0\cdot005$ Å) these values are close to those listed in Table 3 for $GdCu_7$ and, apart from the microscopic observation, show that the compound $GdCu_7$ has only a relatively small region of homogeneity.

X-ray observations on annealed and quenched samples of various composition between YCu_5 and YCu_7 show that is is not unlikely that the phases YCu_5 and YCu_7 form part of one relatively large homogeneity region and indeed give rise to a situation similar to that observed in some rare earth cobalt systems. A detailed investigation of this point will be the object of a forthcoming study.

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Acta Cryst. (1971). B**27**, 1088

The Structure of the α Form of Uranyl Hydroxide

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(*Received* 13 *April* 1970)

The crystal structure of α-$UO_2(OH)_2$ has been determined from single-crystal X-ray diffraction data. α-$UO_2(OH)_2$ is orthorhombic, space group *Cmca* or *C2cb*, with $a=4\cdot242$ (1), $b=10\cdot302$ (1) and $c=6\cdot868$ (1) Å. Least-squares refinement based on the 199 independent observed reflexions in the range $0<(\sin\theta/\lambda)<0\cdot81$ in space group *Cmca* gives a value of $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ of 0·063. Slight deviations of the oxygen atoms from the levels $x=0$ and $x=\frac{1}{2}$, which are allowed in the alternative space group *C2cb*, were not detectable with these data. Each uranyl group is surrounded by six hydroxyl oxygen atoms in puckered hexagonal configuration. The hexagons are condensed into infinite hexagonal sheets, stacked in layers perpendicular to **b**. There are weak interlayer hydrogen bonds and probable hydrogen atom positions are deduced.

Introduction

The orthorhombic α- and β- forms of uranyl hydroxide have been prepared from UO_3 and water under hydrothermal conditions (Dawson, Wait, Alcock & Chilton, 1956). β-$UO_2(OH)_2$ consists of $UO_2(OH)_4$ octahedra, joined at the corners to form infinite $UO_2(OH)_2$ sheets, which are linked by O–H···O (uranyl) hydrogen bonds (Roof, Cromer & Larson, 1964). The thermal expansion of the β form is anisotropic (Bannister & Taylor, 1970). Harris & Taylor (1962) showed that β-$UO_2(OH)_2$ transforms rapidly into α-$UO_2(OH)_2$ on application