

The Crystal Structure of Th₂Co₇

By K. H. J. BUSCHOW

Philips Research Laboratories, N.V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands

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The intermetallic compound formerly designated as ThCo₃ has been identified as Th₂Co₇. This compound occurs in two allotropic forms: α -Th₂Co₇ is hexagonal (Ce₂Ni₇ type); β -Th₂Co₇ is rhombohedral (Gd₂Co₇ type). Both forms usually occur together. There is some indication of a martensitic type of transformation between the α and β forms. The influence of a varying Co concentration is discussed. Lattice parameters are presented for isostructural rare-earth compounds of the type R₂Co₇.

Introduction

The existence of a phase ThCo₂₋₃ was reported to have been detected by X-ray diffraction by Florio, Baenziger & Rundle (1965). From a study of the thorium-cobalt system over the whole range of composition Thomson (1966) concluded that the phase formerly designated as ThCo₂₋₃ occurs actually at 76 ± 1 at. % cobalt, which is close to ThCo₃. In agreement with the results of Florio *et al.* Thomson indexed the X-ray pattern of this phase on the assumption of a hexagonal unit-cell with lattice constants $a=5.038$ and $c=24.64$ Å. In both investigations, however, the above indexing could not account for all of the observed X-ray reflexions.

In the present work we have investigated the crystal structure and composition of compounds occurring in the Th-Co system for cobalt concentrations between 60 and 80 at. %. We observed only one compound in this concentration region, which has now been identified as Th₂Co₇. This compound occurs in two allotropic forms.

Experimental methods and results

The samples were prepared by arc-melting thorium (99.9% purity) and cobalt (99.9% purity) under a purified argon atmosphere. The alloy buttons were turned over and remelted three times; the loss in weight was negligibly small. The alloy buttons were vacuum annealed for 4 weeks in sintered Al₂O₃ crucibles at 950–1000°C. The X-ray diagrams were obtained from powders of as-cast and annealed samples with a Philips X-ray diffractometer PW 1050/30. Cu K α radiation was employed together with an X-ray monochromator AMR3-202.

For the microscopic examination of the samples standard techniques were used. The Co concentration of the samples that were studied in this investigation was between 60 and 80 at. % Co. Single-phase samples could only be obtained by vacuum annealing with those alloy buttons that contained approximately 77.8 at. % Co; this corresponds to a compound of the formula Th₂Co₇.

The X-ray powder diagram of the annealed sample Th₂Co₇ was found to consist of two sets of reflexions that could be indexed respectively on the basis of a hexagonal lattice with $a=5.03$, $c=24.62$ Å and on the basis of a rhombohedral lattice for which in the hexagonal description $a=5.03$, $c=36.91$ Å.

These results suggest that the compound Th₂Co₇ occurs in two allotropic forms whose crystal structures are closely related. Attempts to obtain one of these forms free from the other one by employing various heat treatments including quenching from high temperatures proved unsuccessful. A sample consisting almost exclusively of the hexagonal form (α -Th₂Co₇) was obtained by using a slight excess of cobalt so that formally only a few per cent of the adjacent compound ThCo₅ would be present after annealing, which, in most cases is beyond its detectability by X-ray diffraction. By applying various amounts of Th in excess we were able to obtain a sample in which the rhombohedral form (β -Th₂Co₇) is dominant but in which it is nevertheless accompanied by large amounts of the hexagonal form. In samples in which both allotropic forms are present, especially in the stoichiometric alloy Th₂Co₇, some of the X-ray reflexion lines exhibited an exceptional broadening. For the reflexions from α -Th₂Co₇ this was observed if l was odd, while in the case of β -Th₂Co₇ broadening was observed for reflexions where l was not a multiple of 3.

The crystal structure of α -Th₂Co₇

A powder diffraction diagram was obtained from a sample which, after vacuum annealing at 950°C for 4 weeks, contained negligible amounts of the phase ThCo₅ in addition to the main phase, *i.e.* the hexagonal allotropic form of the compound Th₂Co₇. The lattice constants were $a=5.030 \pm 0.005$ and $c=24.62 \pm 0.02$ Å. The reflexions 00 l , hhl and hkl with $h-k=3n$, were observed to be absent for odd values of l . Possible space groups are therefore $P6_3/mmc$ and $P62c$.

The results described above strongly suggest that the crystal structure of α -Th₂Co₇ is isotropic with the crystal structure of Ce₂Ni₇ described by Cromer & Larson (1959). For calculating the intensities of the X-ray reflexions the positions of space group $P6_3/mmc$

substitution occurs in every third layer of ThCo_5 units (stacked in the c direction) and is accompanied by a shift of the layers. These layer shifts can give rise to either a hexagonal or a rhombohedral stacking sequence. A schematic representation of the hexagonal and rhombohedral structures is given in Fig. 1.

In the *Experimental* section we mentioned that some of the reflexions of both the α - and β -structure in Th_2Co_7 and also in samples containing a moderate excess of Th exhibit a very distinct broadening. The condition for sharp lines for the reflexions hkl of $\alpha\text{-Th}_2\text{Co}_7$ and $\beta\text{-Th}_2\text{Co}_7$, i.e. $l=2n$ and $l=3n$ respectively, is seen to be closely related to the mode of layer stacking (see Fig. 1). Line broadening involving the above conditions is in fact expected if the layer shifts occur more or less at random, so that instead of a succession of either rhombohedral or hexagonal stacking sequences we have a random mixture of both. It should be emphasized that no significant difference in the line broadening was apparent in samples that had been given a high temperature anneal and those that had not. Evidently the difference in stability of the hexagonal and the rhombohedral stacking is negligibly small. It seems unlikely that the effect of a varying Co concentration will result in a preferential stabilization of one of the modifications. In that case we would expect a region in the Th_2Co_7 range over which the limiting lattice dimensions would be different, in that there would be a marked deviation from the relations $a(\alpha)=a(\beta)$ and $c(\alpha)=\frac{2}{3}c(\beta)$. It is possible, however, that the relative amounts of the phases present in the sample depend on the corresponding nucleation or growth rates, which in turn may be strongly influenced by the nature of the primary phase separating from the melt. For high Co concentrations this is clearly the phase ThCo_5 (Thomson, 1966) but a decrease of the Co concentration employed leads eventually to a suppression of ThCo_5 as the primary crystals separating from the melt.

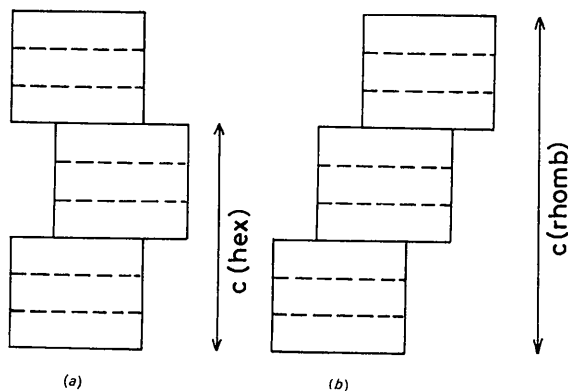


Fig. 1. Schematic representation of the crystal structures of $\alpha\text{-Th}_2\text{Co}_7$ (a) and $\beta\text{-Th}_2\text{Co}_7$ (b). The repeat distances in the c direction are indicated as $c(\text{hex})$ and $c(\text{rhomb})$.

Instead of assuming a random mixture of both types of stacking sequence the observed broadening of the X-ray reflexions could be equally well explained by a microstructure of the sample in which the dimensions of the regions of the α - and β -phases are extremely small in the c direction. Microscopic investigations support this view: it can be seen in Fig. 2 that the microstructure of annealed Th_2Co_7 consists of heavily faulted regions with a high density of lamellae. These lamellae occur in what seem to be the original grains and are strongly reminiscent of a martensitic type of transformation as observed, for instance, in elementary cobalt (Votava, 1961). A martensitic type of transformation in Th_2Co_7 , involving a large thermal hysteresis over the transformation temperature, can account also for the fact that no change in the relative amounts of the α - and β -phase is brought about by annealing or quenching. The presence of a large hysteresis in the transformation is furthermore shown by X-ray diffraction studies at low temperatures. At 80°K the relative amount of the β -modification is increased but the relative amounts of both phases are restored when the sample is brought to room temperature again. When the sample is cooled to 5°K the increase in the amount of the β -phase persists after bringing the sample back to room temperature.

The assumption of a martensitic type of transformation in Th_2Co_7 is also consistent with the observation that the preferential formation of either the α - or β -phase, as a result of the presence of excess cobalt or thorium, still increases within the two-phase regions $\text{Th}_2\text{Co}_7\text{-ThCo}_5$ and $\text{ThCo-Th}_2\text{Co}_7$ respectively. The mechanical properties of samples corresponding to these regions are different and vary continuously with the composition and can therefore strongly influence the martensitic transformation.

A situation similar to the one described above, though somewhat less concentration-dependent, is also encountered with the compounds $R_2\text{Co}_7$ in which R represents a medium-sized rare-earth element, such as Gd or Sm. The metallic radius of the other rare-earth elements is sufficiently smaller or larger for there to be differentiation between the stability of the hexagonal and rhombohedral stacking: for the heavy rare-earth elements we observed the rhombohedral stacking

Table 3. Lattice constants for compounds of the type $R_2\text{Co}_7$

| Compound | a | $c(\text{rhomb})$ | $c(\text{hex})$ |
|--------------------------|---------|-------------------|-----------------|
| Th_2Co_7 | 5.030 Å | 36.91 Å | 24.62 Å |
| La_2Co_7 | 5.101 | 36.69 | 24.51 |
| Ce_2Co_7 | 4.940 | 36.52 | 24.46 |
| Pr_2Co_7 | 5.060 | 36.52 | 24.43 |
| Nd_2Co_7 | 5.059 | 36.43 | 24.39 |
| Sm_2Co_7 | 5.041 | 36.31 | 24.33 |
| Gd_2Co_7 | 5.022 | 36.24 | 24.19 |
| Tb_2Co_7 | 5.008 | 36.18 | present |
| Dy_2Co_7 | 4.992 | 36.13 | not observed |
| Ho_2Co_7 | 4.977 | 36.10 | not observed |
| Er_2Co_7 | 4.960 | 36.07 | not observed |

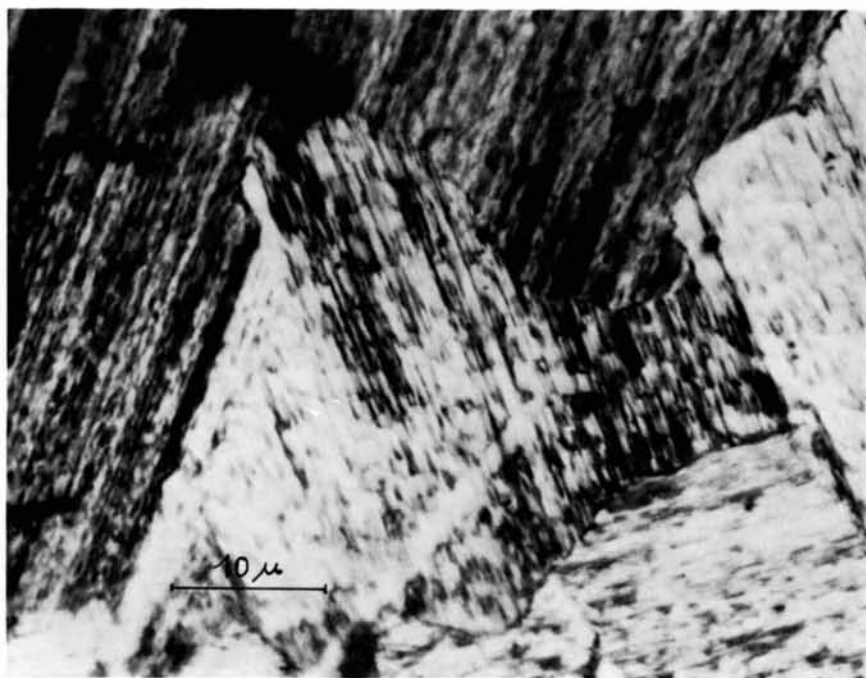


Fig. 2. Microstructure of a sample Th₂Co₇, obtained after etching with dilute HNO₃. (× 2070)

to be stable, while for the light rare-earth elements the hexagonal stacking is stable. In the latter case the rhombohedral form seems to occur as a high temperature modification, which is a situation exactly opposite to that encountered with the two Th₂Co₇ modifications. A survey of the structures occurring and the corresponding lattice constants is given in Table 3. Our values for the rhombohedral form are substantially in agreement with those given by Bertaut *et al.* (1965).

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Solid State Structure and Chemistry of the Choline Halides and their Analogues. Redetermination of the Betaine Hydrochloride Structure, [(CH₃)₃NCH₂COOH]⁺Cl⁻

BY MARK S. FISCHER, DAVID H. TEMPLETON AND ALLAN ZALKIN

Lawrence Radiation Laboratory and Department of Chemistry, University of California, Berkeley, California 94720, U.S.A.

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The crystal structure of betaine hydrochloride, [(CH₃)₃NCH₂COOH]⁺Cl⁻, has been redetermined by X-ray diffraction from the intensities of 782 independent reflections collected on a scanning counter diffractometer. The crystals are monoclinic, space group *P*2₁/*c*, with cell parameters *a* = 7.428, *b* = 9.108, *c* = 11.550 Å, and β = 96.71°. The positions of the hydrogen atoms have been found, and the conventional *R* value has been reduced to 0.026. Final atomic positions differ from those given by Clastre by as much as 0.16 Å. The mean C–N bond length is 1.499 ± 0.004 Å (uncorrected for thermal motion). The cation assumes a completely staggered conformation with the acidic hydrogen atom as far away as possible from the nitrogen atom. The hydrogen bonding from the carboxyl group to the chloride ion is relatively strong compared with the hydrogen bonding in choline chloride.

The structures of choline [(CH₃)₃NCH₂CH₂OH]⁺ X⁻ and betaine [(CH₃)₃NCH₂COOH]⁺ X⁻ compounds are of interest because of both the unusual radiation sensitivity of choline chloride (Tolbert, Adams, Bennett, Hughes, Kirk, Lemmon, Noller, Ostwald & Calvin, 1953) and the frequent occurrence of these compounds in biological systems. They are components of complex lipids, and they can act as transmethylating agents. The related acetylcholine is essential to nerve impulse transfer.

Related structures which have been determined previously include choline chloride (Senko & Templeton, 1960), muscarine iodide (Jellinek, 1957) and acetylcholine bromide (Canepa, Pauling & Sörum, 1966). Clastre (1964) has published a preliminary structure report for betaine hydrochloride, in which he refined the *R* value for two of the two-dimensional projections down to 0.18. Bond distances which we calculated from his pub-

lished atomic coordinates implied that the C–N bond lengths ranged from 1.49 to 1.63 Å in length. We undertook this structure investigation to provide an accurate structure, to locate the positions of the hydrogen atoms, and to investigate the packing.

Experimental

Small colorless crystals of betaine hydrochloride were kindly supplied to us by Dr R. M. Lemmon. These were then recrystallized in the form of colorless needles by the evaporation of a water-methanol solution to dryness at room temperature. The unit-cell dimensions were obtained from careful measurements of the Bragg scattering angles for the *h*00, 0*k*0, and 00*l* reflections, as measured on a manually operated General Electric XRD-5 diffractometer. The α doublet (λ = 1.5405 Å for Cu Kα₁) was resolved for those reflections of highest