Rh₂Sb with (anti)-PbCl₂-Type Structure

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Dedicated to Prof. Dr. D. Babel on the occasion of his 60th birthday

Z. Naturforsch. 45b, 947–951 (1990); received October 2, 1989

Crystal Structure, Crystal Chemistry of PbCl₂-Type Compounds

Rh₂Sb with (anti)-PbCl₂-type structure was reported [11, 12] and RhSb with CoAs₂ (skutterudite) structure [7–10] were reported. The phase diagram by Zhuravlev and Kuz’min [11–13] contains two additional compounds with the approximate compositions Rh₂Sb and RhSb₂. We have grown single-crystals of Rh₂Sb and determined their crystal structure. A preliminary account of our work has appeared [14].

Sample Preparation and Lattice Constants

Starting materials were powders of rhodium (Degussa, 99.9%, 60 mesh) and antimony (99.999%). Microcrystalline samples were prepared by reaction of cold pressed pellets (0.4 g) in evacuated silica tubes. After annealing (2 days at 600 °C followed by 2 days at 800 °C), the samples were quenched, ground to fine powder, cold pressed and annealed again for 2 weeks at 800 °C.

Single-crystals for the structure determination were obtained by reaction of the elemental components using a NaCl/KCl flux, again in evacuated, sealed silica tubes. The starting ratios varied between Rh₂Sb:NaCl:KCl = 2.5:1.2:15:15 and 2:1:1.2:15:15. The samples were annealed for 5 weeks at 800 °C and cooled to room temperature within one day. The flux was dissolved in water. The residuals consisted of needle-shaped crystals of RhSb and elongated prisms of Rh₂Sb, which were identified by their Guinier powder diagrams and by EDAX analyses in a scanning electron microscope. No impurities (heavier than Na) were observed.

The Guinier powder diagrams of the products were calibrated with a-quartz (a = 491.30 pm, c = 540.46 pm) as standard. Rh₂Sb is reported [11, 12] to have a homogeneity range extending from 37 to 39 wt% (33 to 35 at %) Sb. For the phase in equilibrium with Rh, we have found the lattice constants a = 573.6(1) pm, b = 418.1(1) pm, c = 794.9(1) pm, V = 0.1906 nm³. In equilibrium with RhSb we found a = 572.1(1) pm, b = 417.1(1) pm, c = 792.8(2) pm, V = 0.1892 nm³. The evaluation of this pattern is shown in Table I. The phase ~Rh₂Sb₂ was reported to be stable above ~950 °C [11, 12], hence it was not observed in our samples which were annealed at 800 °C.

Structure Determination

The crystal of Rh₂Sb used for the structure determination was taken from a sample, which was in equilibrium with RhSb. It had elongated prismatic shape (10 × 10 × 40 μm³) with the b axis as the main growth direction. Orthorhombic symmetry was established from Weissenberg diagrams. The systematic extinctions (reflections h0l observed only with h = 2n, 0kl only with k+l = 2n) pointed to the space groups Pn₂₃a and Pnma, of which the centrosymmetric group Pnma was found to be correct during the structure refinements. There are four formula units in the cell.

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Verlag der Zeitschrift für Naturforschung, D-7400 Tübingen 0932–0776/90/0700–0947/5 01.00/0

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Intensity data were collected on a four-circle diffractometer with graphite monochromated MoKα radiation, a scintillation counter and a pulse-height discriminator. A total of 1742 reflections was measured in one quarter of the reciprocal space up to 2θ = 90° with θ/2θ scans. The background was determined at both ends of each scan. An empirical absorption correction was applied from ψ scan data. The data were averaged (inner residual $R_x = 0.046$) and reflections with $I < 3σ(I_0)$ were omitted.

From the symmetry, the shape of the unit cell and the composition we guessed that Rh₂Sb might have a PbCl₂-type structure. This proved to be correct. As starting values for the full matrix least-squares refinement we used the positional parameters of Rh₂Si [16]. The atomic scattering factors [17] were corrected for anomalous dispersion [18].

Table I. Guinier powder diagram of Rh₂Sb. The pattern was recorded with CuKα radiation. For the intensity calculation [15] the positional parameters of the structure determination were used. The observed intensities $I_o$ from very weak to very strong are abbreviated: vw, w, m, s, vs. The Q-values are defined by $Q = 100/d^2$ (nm⁻²). Only the observed reflections are listed.

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Table II. Atomic parameters of Rh₂Sb with (anti-)PbCl₂-type structure. All atoms are in position 4c) x, 1/4, z of space group Pnma. The last column lists the equivalent isotropic thermal parameter $B$ (×100, in units of nm²). Standard deviations in the positions of the last listed digit are given in parentheses.

<table>
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<th>Atom</th>
<th>x</th>
<th>z</th>
<th>Beq</th>
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</thead>
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<td>0.0677(2)</td>
<td>0.89(2)</td>
</tr>
<tr>
<td>Rh(2)</td>
<td>0.9591(3)</td>
<td>0.7032(2)</td>
<td>0.81(2)</td>
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<tr>
<td>Sb</td>
<td>0.2861(3)</td>
<td>0.1079(2)</td>
<td>0.75(2)</td>
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</tbody>
</table>

Weights were assigned on the basis of the counting statistics and a parameter correcting the secondary extinction was also refined.

In one series of least-squares cycles the occupancy parameters were allowed to vary. The results gave a slight indication for defects at one rhodium position; occupancies in % with standard deviations in parentheses in the position of the least significant digit: Rh(1): 96.7(6), Rh(2): 101.7(6), Sb: 100.0(5). Nevertheless for the final cycles we assumed full occupancy for all positions. The final conventional and weighted residuals are $R = 0.059$ and $R_w = 0.066$ for 20 variables and 441 structure factors, respectively. The positional parameters and interatomic distances are given in Tables II and III. Listings of anisotropic thermal parameters and structure factors are available [19]*.

Discussion

The PbCl₂-type structure has many representatives. Pearson’s Handbook [20] lists 363 “interme-

* Further details may be obtained from: Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, by quoting the Registry-No. CSD 54376, the names of the authors and the journal citation.
tallic" compounds with this structure. In addition a large number of binary and ternary halides \( \text{MX}_2 \) and \( \text{MXY} \) are known [21–25]. KNaS [26] and the deuteride \( \text{BaD}_2 \) [27] were recently shown to have \( \text{PbCl}_2 \)-type structure. Thus, the \( \text{PbCl}_2 \) structure is very flexible, and the shape of the unit cell and the values of the positional parameters vary greatly. Various axial ratios were used to distinguish the different branches of the \( \text{PbCl}_2 \)-type structure [21, 22, 25, 28–31]. In Fig. 1 we have grouped these.
compounds according to their axial ratios \( a/c \) and \( (a+c)/b \). Historically, the \( \text{Co}_2\text{P} \)-branch (sub-class) with \( c/a \sim 0.85 \) and the \( \text{Co}_2\text{Si} \)-branch with \( c/a \sim 0.70 \) were the first to be distinguished \([28-30]\). The binary and ternary chalcogenides and halides of the main group elements are sometimes ordered into two groups \([22, 25]\): into those like ThS, PbF, PbCl and BaI \([32]\) with relatively large \( b \) axis (and hence small \( (a+c)/b \) ratio), and those like SnBr \([33]\), PbIBr \([34]\) and SbSI \([35]\) with large \( (a+c)/b \) ratio. SnBrCl has a displacive phase transition between both forms with a large hysteresis \([25]\). A group of \( \text{PbCl}_2 \)-type compounds with a relatively narrow existence field is formed by MoGe\(_2\) and the Pnictides (Ti, Zr, Hf, Th)P\(_2\) and (Zr, Hf, Th)As\(_2\) \([20]\). SnClF, where Sn\(^{2+}\) has a stereoactive lone pair \([36]\), and Re\(_2\)P \([37, 38]\), both well established compounds, have axial ratios which separate them from the other \( \text{PbCl}_2 \)-type compounds. Lanthanoid-rhenium carbides Ln\(_2\)ReC\(_2\), where the carbon atoms occupy octahedral voids of the \( \text{PbCl}_2 \)-type structure of the metal atoms, are also known \([39]\).

The structure of \( \text{PbCl}_2 \) may be considered as a distorted version of the hexagonal \( \text{Ni}_2\text{In} \) structure. Actually \( \text{Ni}_2\text{Si} \) \([40]\) and MnCoGe \([41]\) have a \( \text{Ni}_2\text{In} \)-type structure at high temperature, which distorts reversibly on cooling to a low-temperature \( \text{PbCl}_2 \)-type form. The low-temperature forms of \( \text{Ni}_2\text{Si} \) and MnCoGe, however, do not belong to the same branches of the \( \text{PbCl}_2 \)-type structure: MnCoGe belongs to the \( \text{Co}_2\text{P} \)-branch, while \( \text{Ni}_2\text{Si} \) belongs to the \( \text{Co}_2\text{Si} \)-branch. Similarly the \( \text{PbCl}_2 \)-type form of \( \text{Rh}_2\)As \([4, 42]\) (there is another modification of \( \text{Rh}_2\)As which has \( \text{CaF}_2 \)-type structure) with \( c/a = 0.80 \) may be ascribed to the \( \text{Co}_2\text{P} \)-branch, while the presently characterized compound \( \text{Rh}_2\)Sb has an \( a/c \)-ratio of 0.72, which is typical for the \( \text{Co}_2\text{Si} \)-branch.

The two sites for the metal positions in the compounds of these two branches differ greatly. In the compounds of the \( \text{Co}_2\text{P} \)-branch the two metal sites have coordination numbers of about 15 and 12, respectively \([21, 30]\). In \( \text{Rh}_2\)Sb on the other hand, the coordination numbers of the two Rh positions are both 13 (Fig. 2), although it is disputable of how to count the weak Rh(1)–Sb interaction of 317.6 pm.

In counting these as bonding the average Rh(1)–Sb distance is 271.4 pm and the average Rh(2)–Sb distance is 276.4 pm. In addition to the 5 Sb neighbours each Rh atom has 8 Rh neighbours within bonding distance. The average Rh(1)–Rh and Rh(2)–Rh distances are 297.4 pm and 296.6 pm. Thus, the Rh(1) atoms are slightly more strongly bonded to the Sb atoms, and the Rh(2) atoms form on average slightly stronger Rh–Rh bonds. While the \( \text{CaF}_2 \)-type form of \( \text{Rh}_2\)As is diamagnetic, the \( \text{PbCl}_2 \)-type form of \( \text{Rh}_2\)As shows weak temperature independent paramagnetism \([42]\) which, in view of the many Rh–Rh interactions, we interpret as Pauli paramagnetism. Since the band gaps of antimonides are smaller than those of arsenides, we expect \( \text{Rh}_2\)Sb also to have metallic conductivity.

We thank Dr. M. H. Möller for the single-crystal X-ray data collection. We are also indebted to Dr. G. Höfer (Heraeus Quarzschmelze) and Dr. R. Schwarz (Degussa AG) for generous gifts of silica tubes and rhodium metal. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.