Communication

Ordering of Vacancies in Type-I Tin Clathrate: Superstructure of RbSn□

Franck Dubois, and Thomas F. Fssler

2 x 2 x 2 superstructure
$I\,a\,\bar{3}\,d$

$P\,m\,\bar{3}\,n$
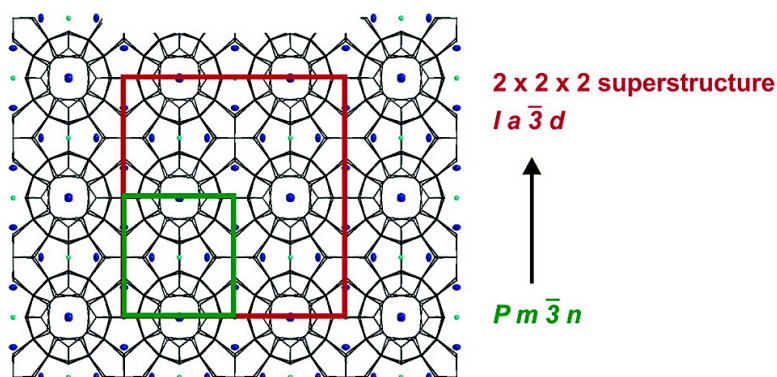
More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 10 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Ordering of Vacancies in Type-I Tin Clathrate: Superstructure of Rb$_8$Sn$_{44}\square_2$

Franck Dubois and Thomas F. Fässler*,$^\perp$

Department Chemie, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received October 27, 2004; E-mail: thomas.faessler@lrz.tum.de

Promising candidates for thermoelectrical materials need to fulfill several criteria: high Seebeck coefficients, good electrical conductors, and finally a thermal conductivity which should be as low as possible.[1,2] The Sn clathrates appear to be promising thermoelectrics.[3,4] Since Sn is heavier than Si or Ge, a Sn-based framework should exhibit a lower thermal conductivity than its Si and Ge counterparts. The thermal conductivity has two contributions, one from the electrical carriers and one from the lattice vibrations. The latter is the most significant contribution, and one way to minimize this variable is to use compounds made from heavy elements.[5] Moreover, the size of the guest cage is larger than that of Si or Ge clathrates, which should lead to a strong "rattling" of the guest atoms and thus to a decrease of the thermal conductivity, as it is observed in Eu$_8$Ga$_{16}$Ge$_{30}$.[6]

Vacancy formation in alkali metal(A)/tin clathrates A$_8$Sn$_{44}\square_2$[7,8] is energetically favored if compared to those with an ideal framework A$_8$Sn$_{46}$.[5,9] The vacancies are located only at one crystallographic site, making this position partially occupied in the primitive clathrate, and they reside on two opposed corners of a six-membered ring. Theoretical calculations show that for K$_8$Sn$_{44}$ the presence of two vacancies within one six-membered ring is the least stable configuration;[9] however, there is no experimental verification of this important question yet. A local ordering of the vacancy should become visible in the form of a superstructure, which has not yet been observed.

The presence of defects in the tetrel network[10] explains the semiconducting behavior of these compounds, since the eight extra electrons donated by the alkali metals are localized at the resulting three-bonded Sn atoms. In the case of Cs$_8$Sn$_{44}$, the Cs atoms do not strongly "rattle" due to the distortion created by the Sn vacancies. As a result, the thermal conductivity of Cs$_8$Sn$_{44}$ shows the temperature characteristic of a typical crystalline insulator.[3] Herein, we present synthesis of Rb$_8$Sn$_{44}\square_2$, where the study of crystalline powders and single crystals show the existence of a 2 × 2 × 2 supercell. The locally relaxed structure due to the presence of Sn vacancies significantly influences displacements of guest atoms. These crystallographic data provide a better understanding of the "rattling" vibration which seems to be the clue to new thermoelectric clathrates ("phonon glass and electron crystal").[11,12]

The type-I clathrate crystallizes in a primitive cubic lattice ($Pm\bar{3}n$, No. 223). The host framework consists of 46 tetrahedrally coordinated atoms, and the arrangement of these atoms leads to the formation of two different cages, namely a pentagonal dodecahedron (with 20 atoms, 12 pentagonal faces [5^{12}]) and a tetrakaidecahedron (with 24 atoms, 12 pentagonal and 2 hexagonal faces [5^{12}6^2]), as shown in Figure 1. The center of each cage is occupied by a guest atom such as alkali or alkaline-earth metal atoms. The crystallographic sites of the tetrahedral atoms are 6c, 16i, and 24k,
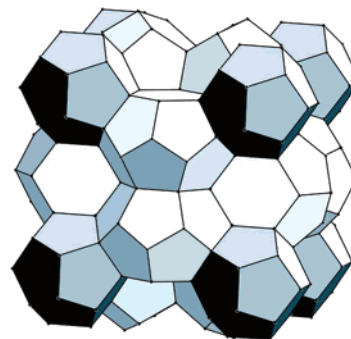

Figure 1. Structure of type-I clathrate with the pentagonal dodecahedron in blue and the tetrakaidecahedron in white.

and those of the guest atoms are 2a and 6d. The 6c site is the partially occupied position in the A$_8$Sn$_{44}$ clathrate.

In the X-ray powder data[13] of a sample obtained from the reaction of the elements, a superstructure was observed.[14] It was resolved by a Rietveld refinement and has been confirmed by a X-ray single-crystal structure refinement.[15] The structure was assigned to the cubic space group $Ia\bar{3}d$, with a unit cell edge of 24.1162(3) Å. This parameter is twice as large as the corresponding value of the primitive cubic clathrate observed previously (12.054(1) Å).[7] During the refinement, we noticed that only the 24c site (Sn6) was partially occupied. Directly attached Sn atoms (Sn4) and next-nearest neighbors (Sn3) were described by split models. After convergence, the R indices were R1 = 0.041 and wR2 = 0.085 for all reflections, and the resulting formula was Rb$_8$Sn$_{43.96(4)}$ or Rb$_8$Sn$_{44}$.

The existence of the supercell is due to an ordering of the vacancies. In the primitive cubic cell, the partially occupied site is distributed around a 4$_2$ axis in a column of tetrakaidecahedra, while it is distributed around a 4$_1$ (or 4$_3$) helical axis in the superstructure (Figure 2). In other words, the partially occupied 6c site in the primitive cubic cell generates two sites in the superstructure, 24c and 24d, with the former being filled by one-third (0.319(4)) and the latter being fully occupied by tin atoms. The partially occupied position leads to a split of the adjacent Sn atoms, Sn4a and Sn4b. The occupation factors of these two split positions refine to one-third (0.32(3)) and two-thirds (0.68(3)), and the values are not due to chance. Indeed, the occupation factor of Sn4a corresponds to that of Sn6. Thus, two alternatives arise: Either Sn6 is fully occupied and bound to Sn4a (situation **I**), or Sn6 is vacant and surrounded by Sn4b atoms (situation **II**, with the ratio **I**:**II** = 1:2).

The Sn3 atom at the ideal position 32e shows, first, short distances to Sn4a (2.69(1) Å) and, second, a larger ellipsoid than those of the other Sn atoms. The splitting of Sn3 in general positions results in three crystallographically equivalent positions Sn3a/b/c and leads to more balanced Sn−Sn distances. Since each Sn3 is bound only to one Sn4a, the atoms are connected in the following way: Sn3a is bound to Sn4a (2.87(1) Å), Sn3b/c to Sn4b (2.879(9) and 2.96(1) Å), and Sn3a/b/c to Sn3a/b/c (2.832(2) Å). Thus, there is no tetrakaidecahedron Rb@Sn$_{24}$ without a vacancy.
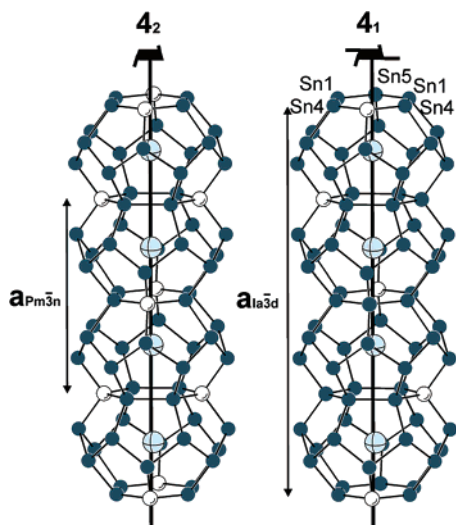
Figure 2. Column of tetrakaidecahedra of the primitive cubic (left) and the superstructure (right) type-I clathrate. White, dark, and blue circles denote partially occupied (Sn6) and fully occupied sites of tin and rubidium, respectively.
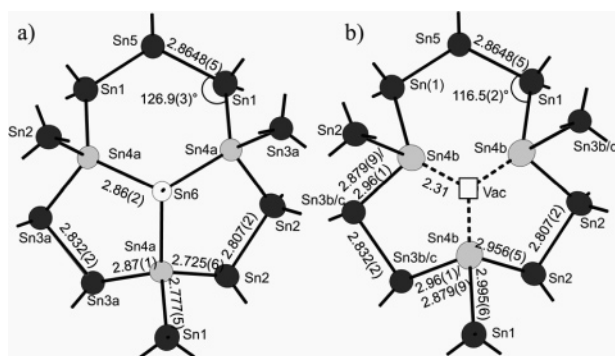

Figure 3. Detail of the Sn framework around the partially occupied Sn6 position ($24c$); Sn4 split into Sn4a and Sn4b, Sn3 ($32e$) split in three equivalent positions Sn3a/b and c. (a) Situation **I** in the neighborhood of Sn6. (b) Situation **II** around the vacancy. Dark, white, and gray circles represent fully occupied sites. All distances are in Å.

Figure 3 depicts a section of the tetrakaidecahedron with related Sn–Sn distances for the two situations **I** and **II**. The distance analysis shows that the Sn–Sn contacts are in agreement with the two models. For **I**, the covalent Sn–Sn contacts are in the range of 2.725(6)–2.87(1) Å and compare to single bonds in elemental α tin. In **II**, the structure locally relaxes, and to compensate for these vacancies, Sn–Sn contacts become longer and are typical of three-bonded atoms: 2.958(5), 2.995(6), and 2.96(1)/2.879(9) Å. The angles in the relaxed situation vary between 94° and 118°, whereas in the ideal clathrate, the range is between 103° and 127°. The distortion is localized at the six-membered ring of the cage. As predicted by Møllnitz et al. for K_8Sn_{44}, the removal of a Sn atom from the six-membered ring leads to the diminution of the Sn5–Sn1–Sn4b bond angles of 6°, we find for Rb_8Sn_{44} 10°.[5]

We noticed that the positions of the Rb atoms in the tetrakaidecahedron are not in the center but are closer to Sn5 opposite to the partially occupied Sn6 site. The anisotropic displacement of Rb2 is twice as large as that of Rb1, which centers the pentagonal dodecahedron, but a split model cannot be deduced from the data. This is in agreement with the observation for $Sr_8Ga_{16}Ge_{32}$ where the Sr atoms in the tetrakaidecahedron "rattle" more strongly.[16,17]

Rb_8Sn_{44} presents the first example of a binary clathrate with a superstructure,[18] and straightforward bulk synthesis will now allow the determination of the thermoelectric properties also for this compound.

Supporting Information Available: Tables of data collection and refinement parameters, positional and anisotropic displacement parameters, distances, and Rietveld refinement; X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Dubois, F.; Fässler, T. F.; *Z. Anorg. Allg. Chem.* **2004**, *630*, 1718.
(2) DiSalvo, F. J. *Science* **1999**, *285*, 703. Tritt, T. M. *Science* **1999**, *283*, 804.
(3) Nolas, G. S.; Chakoumakos, B. C.; Mathieu, B.; Long, G. J.; Weakley, T. J. R. *Chem. Mater.* **2000**, *12*, 1947. Nolas, G. S.; Weakley, T. J. R.; Cohn, J. L. *Chem. Mater.* **1999**, *11*, 2470.
(4) Nolas, G. S.; Cohn, J. L.; Dyck, J. S.; Uher, C.; Yang J. *Phys. Rev. B* **2002**, *65*, 165201−1.
(5) Møllnitz, L.; Blacke, N. P.; Metiu, H. *J. Chem. Phys.* **2002**, *117*, 1302.
(6) Chakoumakos, B. C.; Sales, B. C.; Mandrus, D. G. *J. Alloys Compd.* **2001**, *322*, 127.
(7) Zhao, J.-T.; Corbett, J. D. *Inorg. Chem.* **1994**, *33*, 5721. Dronskowski, R. Ph.D. Dissertation, 1990, Stuttgart, Germany.
(8) Von Schnering, H.-G.; Kröner, R.; Baittinger, M.; Peters, K.; Nesper, R.; Grin, Y. *Z. Kristallogr. - New Cryst. Struct.* **2000**, *215*, 205.
(9) Myles, C. W.; Dong, J.; Sankey, O. F. *Phys. Rev. B.* **2001**, *64*, 165202−1.
(10) Von Schnering, H.-G. *Nova Acta Leopoldina* **1985**, *59*, 168.
(11) Slack, G. A. In *CRC Handbook of Thermoelectrics;* Rowe, D. M., Ed.; CRC Press: Boca Raton, 1995; p 407.
(12) Slack, G. A. *Mater. Res. Soc. Symp. Proc.* **1997**, *545*, 435.
(13) **X-ray Powder Diffraction.** The X-ray powder diffraction data were collected in transmission mode over 4 days (5 to 120° in 2θ) on a STOE diffractometer with a linear PSD detector. A Rietveld refinement was done with Winplotr package.[13a] It is in agreement with the crystal data (cR_{wp} = 0.121, R_{Bragg} = 0.084, χ^2 = 1.77). (a) Roisnel, T.; Rodriguez-Carvajal, J.; *FULLPROF*, version LLB-LCSIM; October 2004, France.
(14) **Synthesis.** $Rb_8Sn_{44}\square_2$ was synthesized by reacting stoichiometric amounts of Rb and Sn in a niobium container which was closed by arc-welding under argon and transferred in a quartz tube. The mixture was heated at 700 °C for 24 h and then slowly cooled to 275 °C at the rate of 3 °C/h. This temperature was dwelt for 2 days, then a slow cooling with a rate of 6 °C/h to room temperature was realized. The powder diffraction shows the presence of extra peak reflections. The compound is air stable, and EDX analysis shows a Rb:Sn ratio of roughly 8:44.
(15) **Structure Determination.** The diffraction data were collected at room temperature on an Enraf-Nonius KappaCCD at the window of a rotating anode (Nonius, FR591) and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods and refined by least-squares with the aid of SHELX 97.[15a] Crystal data: cubic, space group $Ia\bar{3}d$, a = 24.1162(3) Å, V = 14025.8(3) Å³; Z = 8; μ = 20.855 cm^{-1}; ρ_{calcd} = 5.594 g·cm^{-3}; R1/wR2 (all data) = 0.041/0.085 for 1076 reflections. Crystal getting: In the course of reacting oxides with tetrelides such as Si_4^{4-}, Ge_4^{4-}, and Sn_4^{4-} to built up "double salts" intergrowth compounds^b which are stable only in a small temperature range, we found single crystals of $Rb_8Sn_{44}\square_2$. (a) Sheldrick, G. M. *SHELX-97 Program for Crystal Structure Determination*; University of Göttingen, 1997. (b) Hoffmann, S.; Fässler, T. F.; Hoch, C.; Röhr, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 4398.
(16) Chakoumakos, B. C.; Sales, B. C.; Mandrus, D. C.; Nolas, G. S. *J. Alloys Compd.* **1999**, *296*, 80.
(17) Nolas, G. S.; Weakley, T. J. R.; Cohn, J. L.; Sharm, R. *Phys. Rev. B* **2000**, *61*, 3845.
(18) A more complicated superstructure with space group $P4_2/m$ and partial ordering of vacancies at phosphorus sites has been recently observed in $Sn_{14}In_{10}P_{21.2}I_8$. Shatruk, M. M.; Kovnir, K. A.; Lindsjö, M.; Presniakov, I. A.; Kloo, L.; Shevelkov, A. V. *J. Solid State Chem.* **2001**, *161*, 233.
(19) Carrillo-Cabrera, W.; Budnyk, S.; Prots, Y.; Grin, Y.; *Z. Anorg. Allg. Chem.* **2004**, *630*, 2267.

JA043500R