the $IO_2F_2^-$ ion seems to increase when a formal positive charge is placed on iodine in iodyl compounds and polymerization may occur not only *via* polycation formation as speculated previously[11,14,21] but also *via* bridging anionic groups. It is obvious that under such circumstances the calculation of iodine–oxygen stretching force constants is not too meaningful.

An additional difference in chemical behavior between IO_2F and IO_2SO_3F was found when attempts were made to prepare the KIO_2F_2 analog $KIO_2(SO_3F)_2$ *via* the reaction $KIO_3 + S_2O_6F_2 \rightarrow KIO_2(SO_3F) + 0.5O_2$. Even though a reaction took place and the white reaction product obtained analyzed as $KIO_2(SO_3F)_2$, the recorded Raman spectrum revealed the presence of a stoichiometric mixture of KSO_3F and IO_2SO_3F. This indicates that IO_2SO_3F does not act as an SO_3F^- acceptor. This conclusion should have some bearing on the interpretation of the conductometric results.

It became interesting to see whether a strongly ionizing solvent as HSO_3F would be capable of breaking up the polymeric structure of IO_2SO_3F. Quite in contrast to other fluorosulfates which have been studied by us, iodyl fluorosulfate dissolves extremely slowly. Even for small amounts, several hours is required before a clear solution is formed. A similar observation was made when the polymeric solute $Sn(SO_3F)_4$[38] was dissolved, indicating a slow breaking up of a polymeric species.

The solutions of IO_2SO_3F were found to be conducting and the maximum concentration was about 4×10^{-2} mol/kg, comparable to the concentration range studied by Gillespie and Senior.[14] The resulting experimental and interpolated electrical specific conductivities are listed in Table IV for both IO_2SO_3F and the reference base KSO_3F. A specific conductivity plot *vs.* molality is shown in Figure 3. The following features are noteworthy. Compared to KSO_3F and ClO_2SO_3F,[21] iodyl fluorosulfate is not completely dissociated into $IO_2{}^+{}_{solv}$ and SO_3F^-, even at very low concentrations. The observed κ values indicate a more extensive ionic dissociation than observed for HIO_3 in H_2SO_4,[14] which may well be due to the higher acidity of HSO_3F. The specific conductance *vs.* molality plot shows appreciable curvature. Even though addition of KSO_3F results in an immediate increase in specific conductance—no minimum is observed—the slope of the resulting curve is less steep than that found for KSO_3F itself, indicating some uptake of SO_3F^- and a repression of the original ionic dissociation presumably under formation of SO_3F-bridged polymeric cationic fragments.

In conclusion our experimental findings are in good agreement with previous work by Gillespie and Senior.[14] In addition to the proposed polymeric oxygen-bridged structures,[14] a structural model where discrete IO_2 groups are bridged by bidentate fluorosulfate groups becomes a possible alternative, which can account for the observed conductivities. Unfortunately no meaningful Raman spectra could be obtained on such dilute solutions.

Acknowledgment.—We are grateful to Mr. A. M. Qureshi for his help in obtaining some of the Raman spectra and to Mr. Steve Rak for building the glass reactor used in the preparative part of this study. Financial support from the National Research Council of Canada is gratefully acknowledged.

Contribution from the Reactor Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830,
and the Materials Science Laboratories, Department of Chemical Engineering,
University of Texas at Austin, Austin, Texas 78712

The Crystal Structure of β-Ytterbium Triantimonide, a Low-Temperature Phase[1]

By G. D. BRUNTON and H. STEINFINK*

Received February 11, 1971

A previously reported phase Yb_5Sb_2 is shown to be a low-temperature polymorph of Yb_5Sb_3. β-Yb_5Sb_3 crystallizes in the orthorhombic system, space group *Pnma*, $a_0 = 12.398\ (2)$ Å, $b_0 = 9.562\ (2)$ Å, and $c_0 = 8.246\ (2)$ Å, $Z = 4$, $\rho_{calcd} = 8.343$ g/cm³. Molybdenum radiation was used to measure the integrated intensities of 1555 independent reflections with a scintillation counter and a four-circle diffractometer. The parameters were refined by least squares to $R = 0.0797$ for 1252 reflections greater than σ using anisotropic temperature factors. The structure consists of trigonal prisms formed by Yb whose centers are occupied by Sb. The prisms articulate by edge sharing into hexagons, and by face sharing they form hexagonal columns parallel to [010]. Within the columns are rhombs formed by two Yb and two Sb, and the Sb atoms are shared with the next rhombs to produce an infinite chain. The structure is very closely related to Rh_5Ge_3. The shortest Yb–Yb bond length is 3.543 Å and the shortest Yb–Sb distance is 3.044 Å. There is only a tenuous relationship between the structures of the high-temperature α form and the low-temperature β form.

Introduction

Seven intermediate phases have been reported to exist in the Yb–Sb phase diagram,[2] and five had known crystal structures. The stoichiometries of the two phases whose structures were new were given as Yb_5Sb_4 and Yb_5Sb_2. A single-crystal structure determination showed that the former compound had the composition $Yb_{11}Sb_{10}$ and was isostructural with $Ho_{11}Ge_{10}$.[3,4] A pre-

---

[1] Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

[2] R. E. Bodnar and H. Steinfink, *Inorg. Chem.*, **6**, 327 (1967).

[3] H. L. Clark, H. D. Simpson, and H. Steinfink, *ibid.*, **9**, 1962 (1970).

[4] G. S. Smith, Q. Johnson, and A. G. Tharp, *Acta Crystallogr.*, **23**, 640 (1967).

TABLE I

ATOMIC PARAMETERS FOR β-Yb_5Sb_3 (PARAMETERS × 10^4)

Atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Yb(1)	740 (1)[b]	421 (1)	1952 (2)	24 (1)	18 (1)	30 (2)	−1 (1)	−9 (1)	−0 (1)
Yb(2)	2295 (1)	$^1/_4$	8196 (2)	15 (1)	28 (2)	30 (3)	0	−5 (1)	0
Yb(3)	54 (1)	$^1/_4$	5354 (2)	14 (1)	27 (2)	20 (2)	0	1 (1)	0
Yb(4)	2883 (1)	$^1/_4$	3492 (2)	15 (1)	33 (2)	29 (2)	0	−4 (1)	0
Sb(1)	4834 (2)	$^1/_4$	5786 (3)	14 (1)	16 (2)	19 (3)	0	−4 (2)	0
Sb(2)	3293 (1)	4856 (2)	675 (2)	14 (1)	20 (2)	26 (2)	−1 (1)	3 (1)	−3 (2)

[a] Coefficients in the temperature factor: $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [b] The number in parentheses is the standard error in terms of the last significant digit, as derived from the variance–covariance matrix.

liminary report on the structure of Yb_5Sb_2[5] indicated that, from a consideration of unit cell volume and density, there could be 28–32 atoms in the cell; this range of atoms was within experimental error of the preparation of the compound, and there was an indication of a homogeneity range for this phase. We have determined the crystal structure of this phase and find that the stoichiometry corresponds to Yb_5Sb_3. This material is thus a low-temperature form of the previously reported Yb_5Sb_3 phase which has the $D8_8$ (Mn_5Si_3) structure type.

Experimental Section

The preparation of this material has been previously described.[2] Small single crystals can be selected from the reaction product without difficulty. An acicular crystal of β-Yb_5Sb_3 with dimensions 0.146 × 0.026 × 0.039 mm was mounted on a computer-controlled Picker four-circle goniostat, set at a 4° takeoff angle, and three-dimensional diffraction intensities to $2\theta = 60°$ were measured with a scintillation-counter detector using unfiltered Mo Kα radiation. The lattice constants were determined from a least-squares refinement of 12 Mo Kβ reflections (λ(Mo Kβ) 0.63225 Å) in the range $2\theta = 20$–$30°$, yielding $a_0 = 12.398$ (2), $b_0 = 9.562$ (2), and $c_0 = 8.246$ (2) Å, $Z = 4$, $\rho_{\text{calcd}} = 8.343$ g/cm^3. A total of 1555 independent reflections were measured of which 1252 were greater than σ and 923 were greater than 2σ; σ is the estimated standard error of each individual reflection. An angular scan range of 1.0° was step scanned in increments of 0.01° with 2-sec counts at each step, and the background was measured on each side of the peak for 120 sec. A standard reflection, (400), was used throughout the data collection to check on intensity drift. One measurement of the standard intensity was assigned unit value and all others were expressed as fractions of this value. The intensities obtained between two successive measurements of the standard reflection were multiplied by the appropriate fraction so that all measured intensities were referred to a single value of the (400) intensity. The data were corrected for Lorentz and polarization effects and for absorption ($\mu = 577.69$ cm^{-1}).[6] The diffraction symmetry is mmm and the conditions for reflection are $hk0$, $h = 2n$, and $0kl$, $k + l = 2n$, which is consistent with space groups $Pnma$ and $Pn2_1a$. A Wilson plot indicated that the structure was probably centric and the structure confirms this assumption.

Structure Determination

Initial parameters for about two-thirds of the atoms in the asymmetric unit were determined from an E map calculated from $E(hkl)$'s whose signs were determined by a direct-method program. The program determines signs by iterative application of Sayre's equation and was written by Long.[7] The positions of all of the atoms were determined from Fourier and difference Fourier maps and the structure was refined by a least-squares procedure using a modification of ORFLS.[8] The quantity minimized was $\Sigma w(F_o^2 - F_c^2)^2$ with weights, w, equal to the reciprocals of the variances which were estimated from the empirical equation

$$\sigma^2(F_o)^2 = [T + B + [0.03(T - B)]^2]/A(Lp)^2$$

where T is the total count, B is the background count, A is the absorption, and Lp is the Lorentz–polarization expression.[9] The atomic scattering factors for Yb and Sb were taken from Cromer and Waber[10] and the anomalous dispersion terms for Mo Kα radiation were taken from Cromer.[11] Table I contains the final atomic parameters obtained from a least-squares refinement based on 1252 reflections greater than σ. The discrepancy indices for the final structure factors, Table II,[12] are as follows: for all 1555 reflections, $R = 0.100$, $wR = 0.134$; for 1252 reflections greater than σ, $R = 0.0797$, $wR = 0.133$; for 923 reflections greater than 2σ, $R = 0.0599$, $wR = 0.127$ $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|, wR = [\Sigma w(F_o^2 - F_c^2)^2]^{1/2}/[\Sigma(F_o^2)^2]^{1/2}\}$. The standard deviation of an observation of unit weight $[\Sigma w(F_o - F_c)^2/(n_0 - n_v)]^{1/2}$ is 1.92 where $n_0 = 1252$ is the number of reflections and n_v the number of variables, 44. An extinction correction was applied to F_c by the method suggested by Zachariasen.[13] A refinement using the acentric space group $Pn2_1a$ yielded discrepancy indices for the various groups of reflections that were 0.02–0.025 higher than for the comparable centric refinements.

Discussion

The structure of this alloy can be described in terms of layers of atoms perpendicular to [010]. Yb(1) and Sb(2) atoms form one such layer between $y = -0.04$ and $+0.04$. The Sb(2) atoms form hexagons whose edge is about 4.4 Å and their centers are at the centers of inversion. Within each hexagon and symmetrically disposed about the center of inversion are two Yb(1) atoms. Within this layer each Sb(2) is surrounded by three Yb(1) atoms at distances of 3.34, 3.35, and 3.62 Å. The distance between the two Yb(1) atoms within the hexagonal ring is 3.79 Å. This layer of Yb(1) and Sb(2) atoms is sandwiched between two layers of atoms consisting of Yb(2), Yb(3), Yb(4), and Sb(1), at $y = +^1/_4$ and $y = -^1/_4$. The Yb atoms within a level form distorted triangles whose edges vary from 3.62 to 4.43 Å and they in turn share corners to form distorted hexagons. Within a hexagon, but offset from the center, is one Sb(1) atom. Within a layer, Yb(2) is surrounded by two Yb(3) atoms at 3.624 and 3.635 Å, two Yb(4) atoms at 3.947 and 4.428 Å, and two Sb(1) atoms at 3.165 and 3.723 Å; Yb(3) is surrounded by five neighbors consisting of two Yb(4) atoms at 3.829 and 4.160 Å and two Yb(2) atoms and one Sb(1) atom at 3.195 Å; Yb(4) has five nearest neighbors consisting of two Yb(2) atoms, two Yb(3) atoms, and one Sb(1) atom at 3.071 Å;

---

(5) A. Raman and H. Steinfink, *Acta Crystallogr., Sect. A*, **21**, A86, (1966).

(6) D. J. Wehe, W. R. Busing, and H. A. Levy, USAEC Report ORNL-TM 229, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(7) R. E. Long, Doctoral Dissertation, University of California at Los Angeles, Los Angeles, Calif., 1965.

(8) W. R. Busing, K. O. Martin, and H. A. Levy, USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(9) G. M. Brown and H. A. Levy, *J. Phys. (Paris)*, **25**, 397 (1964).

(10) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18** ,104 (1965).

(11) D. T. Cromer, *ibid.*, **18**, 17 (1965).

(12) Table II, a listing of structure factor amplitudes, will appear immediately following this article in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

(13) (a) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967); (b) W. H. Zachariasen, *ibid.*, *Sect. A*, 24, 212 (1968).

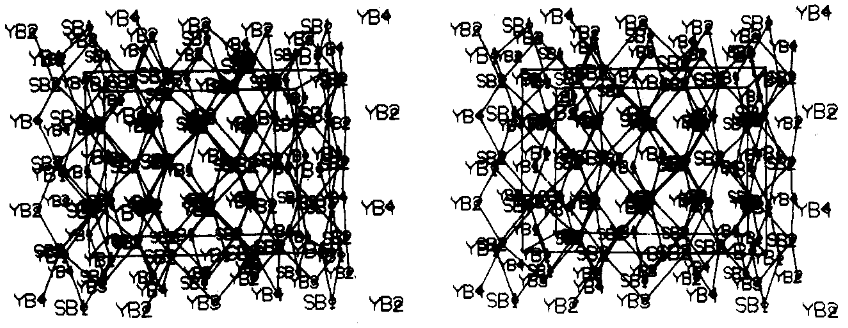

Figure 1.—Stereoscopic view of β-Yb_5Sb_3. The a_0 axis is horizontal and b_0 is vertical.

the Sb(1) atom has four Yb near neighbors. The layer at $y = -{}^1/_4$ has the same arrangement and is related by inversion centers to the $y = {}^1/_4$ level.

The Yb atoms in the layers $y = {}^1/_4$ and $-{}^1/_4$ form trigonal prisms and the Sb(2) atoms in the $y \cong 0$ level are approximately at the centers of these prisms. The edge of the prism parallel to [010] is equal to ${}^1/_2b$. The three-dimensional framework that is formed by this arrangement consists of hexagonal columns parallel to the *b* axis and within the hexagonal column is a chain of rhombs formed by Yb(1) and Sb(1) atoms parallel to the *b* axis, Figure 1. The rhombs formed by the Sb(1)–Yb(1) atoms are 3.04 and 3.21 Å on edge, the Sb(1)–Yb(1)–Sb(1) angle is 105.4°, and the Yb(1)–Sb(1)–Yb(1) angle is 74.6°. Table III lists bond distances around the atoms and they are similar to those observed in other Yb–Sb phases.[2,3] The crystal structure of this phase is almost identical with that of Rh_5Ge_3[14,15] except that there are slight distortions in Yb_5Sb_3 which cause the a_0 axis dimension to be larger than would be expected merely because of the change in size of the respective atoms.

TABLE III

BOND DISTANCES IN β-Yb_5Sb_3[a]

Atoms	Dist, Å	Atoms	Dist, Å
Yb(1)–Sb(1)	3.039 (2)	Yb(2)–Sb(2)	3.284 (2)
Yb(1)–Sb(1)	3.211 (3)	Yb(2)–Sb(2)	3.353 (2)
Yb(1)–Sb(2)	3.340 (2)	Yb(2)–Yb(3)	3.624 (2)
Yb(1)–Sb(2)	3.346 (2)	Yb(2)–Yb(3)	3.634 (3)
Yb(1)–Yb(3)	3.542 (2)	Yb(2)–Sb(1)	3.722 (3)
Yb(1)–Yb(4)	3.553 (2)	Yb(2)–Yb(4)	3.947 (3)
Yb(1)–Sb(2)	3.620 (2)	Yb(3)–Sb(1)	3.194 (4)
Yb(1)–Yb(3)	3.702 (2)	Yb(3)–Sb(2)	3.250 (2)
Yb(1)–Yb(1)	3.792 (3)	Yb(3)–Sb(2)	3.266 (2)
Yb(1)–Yb(2)	3.846 (2)	Yb(3)–Yb(4)	3.829 (3)
Yb(1)–Yb(1)	3.975 (3)	Yb(4)–Sb(1)	3.071 (3)
Yb(1)–Yb(4)	4.078 (2)	Yb(4)–Sb(2)	3.275 (3)
Yb(2)–Sb(1)	3.165 (3)	Yb(4)–Sb(2)	3.430 (2)

[a] Numbers in parentheses are standard deviations.

The solution of the structure fixes the stoichiometry of this previously designated Yb_5Sb_2 phase as a low-temperature form of Yb_5Sb_3 which is now labeled as the β form. In the $D8_8$ structure the metalloid atoms form a very distorted octahedron with a metal atom in the center, and these link to form hexagonal columns parallel to [001]. Within the columns are octahedra of metal atoms. In the β form trigonal prisms are formed by the metal atoms and the array of atoms inside the hexagonal columns is different. Thus a similarity between the two structures can only be introduced if the atomic species which make up the three-dimensional framework are ignored (or interchanged).

The diamond-shaped chain of Yb(1) and Sb(1) atoms in the channels of the β structure could be considered as nonessential to the stability of the structure and the removal of some of the atoms could account for the range of homogeneity that was considered to exist for this compound. In the refinement of the structure the occupancy factors for these two sites were varied and invariably the refinement terminated with full occupancy. Any attempt to vary the scattering power in those sites always resulted in significantly larger discrepancy indices. Thus it is concluded that the crystal which was analyzed had the 5:3 stoichiometry. The previously indicated range of homogeneity might be misleading since in the preparation from the elements some of the starting materials might not participate in the reaction because of their volatility. After the structure was established, we synthesized this material from a 5:3 starting mixture of Yb–Sb and obtained powder patterns identical with the one previously published.[2] Several preparations in which the ratios of the starting components varied always produced materials which gave the β-Yb_5Sb_3 powder diffraction pattern, and only when the starting composition exceeded 37.5% Sb was the presence of Yb_4Sb_3 detected. It must, therefore, be concluded that this is a low-temperature phase with stoichiometry Yb_5Sb_3 and that it is probably a line compound.

(14) S. Geller, *Acta Crystallogr.*, **8**, 15 (1955).

(15) K. Schubert, "Kristallstructuren zweikomponentiger Phasen," Springer-Verlag, Berlin, 1965, p 324.