AN X-RAY CRYSTALLOGRAPHIC INVESTIGATION OF A PHASE IN THE YTTERBIUM(III) -- OXIDE -- CHLORIDE SYSTEM

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ABSTRACT

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by

John Thomas Richards

A phase which is a probable oxidechloride of ytterbium (III) was prepared and has been investigated. The green plate-like cyrstals were found to exhibit hexagonal symmetry and belong to space group $P\bar{6}2m$. The observed lattice parameters are a = $6.187_9 \pm 0.001_6$ Å and c = $19.76_4 \pm 0.01_5$ Å. A partial structural determination locates the 16 metal atom positions in the unit cell along with the approximate positions for 19 oxygen atoms. Chemical arguments are used to construct a complete model for the structure of this phase: $(Yb_2O_3)_6(YbOC1)_4$.

This phase was isolated as a side reaction product from an attempted preparation of an ytterbium chloride phase. The oxidechloride probably resulted from the presence of traces of water.

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CHAPTER I

INTRODUCTION

Ytterbium exists in two stable oxidation states-divalent and trivalent. The halides of these two states are readily prepared¹ and their structures have been determined²⁻⁴. Recent attention has been focused on the halides of the other lanthanide series elements to study their less stable reduced oxidation states⁵⁻⁸.

In the course of investigating the phase diagrams of the lanthanide series halides, Corbett, *et al.*, have detected many previously unknown phases of mixed oxidation states; that is, phases composed of combinations of valence states. As an example, the gadolinium-gadolinium trichloride phase diagram⁵ indicates the presence of a phase of composition $GdCl_{1.58}$. The crystal structure of this phase has been solved⁶ and is interpreted by Corbett to be a mixture of gadolinium metal atom clusters and gadolinium trichloride.

While phases of mixed oxidation states are reported for the earlier members of the lanthanide series elements, Fishel and Eick report⁹ the existence of the same type of phases in the ytterbium dichloride-ytterbium trichloride system. They report the composition as being $YbCl_{2.26}$, detected as the product of a partial hydrogen reduction of $YbCl_3$.

The purpose of this research was to characterize YbCl_{2.26} or another ytterbium chloride phase of intermediate

oxidation state by single crystal structural methods. Of particular interest to the ytterbium system is the thuliumthulium(III) chloride phase diagram⁸ because of the similarities known¹ to exist between the chemistry of ytterbium and thulium. One of the more interesting results of Caro and Corbett's phase study is the postulated existence of at least seven phases in the composition range $TmCl_{2.04}$ to $TmCl_{2.12}$, detected by thermal inflections in the cooling curves at constant compositions. These phases were interpreted to result from an ordering of a Tm(II) rich crystal lattice to include progressively more Tm(III) with the creation of cation vacancies and the addition of interstitial anions.

The relevance of the thulium system to this work can be seen in Table 1, which is a listing of crystallographic data for TmCl_3^4 , YbCl_3^4 , TmCl_2^8 and YbCl_2^2 . It is evident that Table 1: Crystal Data for Ytterbium and Thulium Chlorides

Compound	Symmetry and Structure Type	a	Ъ	С	β
TmCl ₃	Monoclinic AlCl ₃	6.75 Å	11.73 Å	6.39 Å	110.6°
чьс1 ₃	Monoclinic AlCl ₃	6.74	11.66	6.38	110.4
TmC12	Orthorhombic CaF ₂	6.55	6.68	6.93	
чьс1 ₂	Orthorhombic CeSI	6.69	13.15	6.94	

there is a very close structural relationship between the dichlorides and trichlorides of thulium and ytterbium. The major discrepancy in the lattice parameter b between TmCl₂

and YbCl₂ is a result of Fishel's reindexing YbCl₂ from the fluorite to the CeSI structure type, done on the basis of single crystal structural data. Döll and Klemm¹⁰ had initially erroneously indexed YbCl₂ on a fluorite structure type and obtained the lattice parameters: a = 6.53 Å, b =6.68 Å, c = 6.91 Å. On the basis of the good agreement of Döll and Klemm's lattice parameters with those of TmCl₂, the close structural relationship with YbCl₂ is now more apparent. Fishel reindexed YbCl₂ from fluorite to the CeSI structure type because the cation to anion radius ratio and the axial ratios a/c and b/c more closely match the latter structure type, and suggested TmCl₂ might also be better indexed on the CeSI structure type.

If the conclusion of Caro and Corbett is correct and the many phases in the Tm-TmCl₃ systems are the result of successive modifications of the dichloride lattice, then the close crystal similarity between the thulium and ytterbium systems indicates the probable existence of several phases of intermediate stoichiometry between YbCl₂ and YbCl₃. Any of these expected phases which could be prepared as single crystals suitable for X-ray structural analysis would satisfactorily meet the stated goal of characterizing this system.

For the previously mentioned phase YbCl_{2.26}, Fishel was unable to obtain single crystals for analysis². Thus a different approach was chosen to prepare a reduced phase, to obtain the single crystals that apparently could not be found in the product of Fishel's hydrogen reduction.

CHAPTER II

EXPERIMENTAL

Two reaction procedures were followed for the preparation of the intermediate phase $YbCl_{2.26}$: 1) a mixture of ytterbium metal and ytterbium trichloride confined in a sealed ampoule was heated to temperatures between 550 and 1450°C (various runs) and 2) a mixture of ytterbium dichloride and trichloride confined in a sealed tantalum ampoule was heated to a temperature of 800°C. These temperatures were chosen as being less than, equal to and greater than the melting points of the reactants (the metal, dichloride and trichloride melt in the range 700 to 865°C).

A consistent heating procedure was used in all preparations. The reactants were cycled to temperature over a period of eight hours, heated at temperature for periods of time which varied from 1.5 to 13 days, then cooled to room temperature over a period of eight hours. In some preparations carried out by the first procedure, a very small amount of iodine was included to serve as a transport agent; iodine was present in all preparations carried out by the second procedure.

Ytterbium trichloride was prepared according to the method of Taylor and Carter¹¹. The overall reaction is as follows:

 $Yb_2O_3 + 6NH_4C1 = 2YbC1_3 + 3H_2O_3 + 6NH_3(g)$ (1).

Briefly, the method entails dissolving a six-fold excess of ammonium chloride with the sesquioxide and coprecipitating the hydrated trichloride and ammonium chloride from evaporating hydrochloric acid. The dried mixture is heated under a stream of inert gas at 200° C for 1.5 hours, then at 430° C for eight hours. The product is heated to above 500° C before cooling.

Ytterbium dichloride was prepared according to the method of De Kock and Radtke¹². The overall reaction is as follows:

 $2YbCl_3 + 2Zn + 2NH_4Cl = 2YbCl_2 + 2ZnCl_2 + 2NH_3g + H_2g(2)$. Zinc metal and zinc chloride are added to YbCl_3 to provide a reducing melt (mole ratios: $ZnCl_2/YbCl_3 = 1.2$, $NH_4Cl/YbCl_3$ = 12, $Zn/YbCl_3 = 2$). The reaction temperature is increased to over $500^{\circ}C$ and maintained at that temperature for more than an hour until a clear melt is obtained. The crude product is purified by sublimation at $1300^{\circ}C$ under high vacuum.

Routine analyses of the trichloride and dichloride prepared by these methods were effected by an X-ray powder diffraction technique. An 80 mm Guinier forward focusing camera which employed Cu Ka radiation was used. Platinum powder (a = 3.9237 ± 0.0003 Å) was included in the samples for powder diffraction analysis. The interplanar d-spacings of the powder patterns are based on this platinum standard.

X-ray fluorescence experiments were performed with a Norelco spectrometer which used a graphite analyzing crystal and a tugsten anode tube. Three targets were used:

platinum, aluminum and quartz. Quantitative analyses were not attempted, only the qualitative presence of metals was examined.

Both the ytterbium dichloride and trichloride are hygroscopic materials¹ and must be isolated from atmospheric moisture. Additionally, it was assumed that all intermediate phases in the dichloride-trichloride system would behave similarly. All transfer of materials was performed in a dry box under a dried argon atmosphere and at all other stages of experimental work precautions were taken to isolate the experiment from atmospheric moisture.

CHAPTER III

X-RAY STRUCTURAL ANALYSIS

The single crystal diffraction experiment consists of measuring the intensity of a diffraction maximum and recording its position in space relative to the orientation of the crystal. The maxima can be viewed as arising from a reflection of the incident X-ray beam off of planes of atoms in the crystal and are thus referred to as "reflections." These reflections are in turn indexed by three integers, hkl, the Miller indicies. The reflection plane is located in the unit cell of dimensions a,b,c by the points a/h, b/k, and c/l.

One parameter that cannot be measured in the diffraction experiment is the phase relationship between the incident and diffracted radiation. This is the so-called "phase problem"¹³ in X-ray structural determination: without the phasing information the structure cannot be derived directly from the experiment.

From a structural model of the contents of a unit cell, the diffraction pattern for the crystal can be computed. These predicted reflections, or structure factors, are dependent on the nature and arrangement of the diffracting material and include phasing information. A measure of the precision by which the structural model matches the crystal structure is provided by the following function:

$$R = \frac{\Sigma ||F_0| - |F_c||}{\Sigma ||F_0|}$$
(3).

where F_0 is the amplitude of the observed reflection and F_c is the calculated structure factor for that reflection.

Because the system being investigated in this research contains heavy metal atoms, the method employed to derive a model structure for the crystal was to compute a Patterson function¹³. The Patterson function, or map, is calculated from $|F_0|^2$ which are independent of the phasing. This map shows positions and magnitudes of vector peaks in the vector space u,v,w corresponding to the real space a,b,c. The peak heights are proportional to the products of the number of electrons at the ends of the vectors, so when heavy and light atoms are both present in the unit cell, the relative orientations of the heavy atoms can be derived from the locations of the most intense vector peaks.

The structure factors calculated from a derived model are the Fourier transforms of the electron distribution within the unit cell, the atoms assumed to be located at the centers of electron density. Electron density maps or Fouriers can be calculated, then, from the calculated structure factors and phasing information. A difference Fourier is synthesized from calculated phases and the difference series between F_0 and F_c . This difference map may be taken to indicate where electron density is too large or where electron density should be increased. A least squares refinement of the atomic positions and temperature factors simultaneously varies these parameters to minimize the R function. The temperature factors (or B values) are measures of the extent to which atomic motion causes the electron density to be more diffuse than in a stationary atom. One B value implies that this motion is being approximated in three dimensions by a sphere, six B values indicate that the six-parameter general ellipse is being used. As opposed to the pecision indicated by the R function, the temperature factors indicate the accuracy of an atomic position. Negative B values may have no meaning; very large B values are suspect also. As an example applicable to this research, Fishel reports B values between -0.9 and 4.4 for the structure of YbCl₂².

Calculations were performed using a Control Data 6500 computer. Least squares refinement (LSQXTL), Patterson function and Fouriers (CRYSTAL) were calculated from programs provided by A. Zalkin. Adaptations were made to use these programs on the CDC 6500.

RESULTS

The results of the attempted preparations of an intermediate phase were examined visually under a microscope. Typically, the Yb/YbCl₃ reaction products included unreacted ytterbium metal, a black compound of unknown composition and colorless to light green crystals of no repetitive morphology. The results of the YbCl₂/YbCl₃ preparations were unclear, the product being composed of the same green crystals (YbCl₂) and white powder (YbCl₃) that were the reactants. Seven preparations were run, five of the Yb/YbCl₃ type and two of the YbCl₂/YbCl₃ type.

When suitable crystals were found, they were mounted on an X-ray precession camera for preliminary investigation. A suitable crystal was taken to mean one that was visibly single and was of an unrecognized type.

One of the colorless crystals was chosen first for examination and was eventually identified from the unit cell parameters and space group as YbCl₂. The orthorhombic unit cell of this crystal yielded lattice parameters of a = 6.70 ± 0.08 Å, $b = 13.2 \pm 0.1$ Å and $c = 6.9_6 \pm 0.1_2$ Å. The space group was Pbca. Bärnighausen, Pätow and Beck report³ values for these parameters to be a = 6.698 Å, b = 13.139 Å, c =6.948 Å, space group Pbca. This result, together with the ytterbium metal observed in the product, indicates incomplete reaction in these preparations. Close examination of all the samples prepared showed only one to contain crystals of a type different from $YbCl_2$. This preparation consisted of metal and trichloride mixed in $YbCl_{2.26}$ stoichiometric proportions with a small chip of iodine (mole ratio: total $Yb/I_2 > 300$) added to the tantalum ampoule before it was welded shut. The temperature was raised to $1000^{\circ}C$ and held there for two hours, then maintained at $800^{\circ}C$ for five days. Aside from the unreacted metal and the recognizable dichloride, there was a small number of green plate-like crystals. The total yield of this type of crystal was estimated to be approximately a milligram.

The majority of these crystals could be seen as twinned by means of the platelets being stacked on top of each other. Several others were only verified as twinned by precession X-ray photography. One good crystal was found for a structural determination $(0.24 \times 0.14 \times 0.056 \text{ mm})$ and was mounted and sealed in a glass capillary to seal out atmospheric moisture.

The precession photographs of this crystal were found to be consistent with a hexagonal unit cell with lattice parameters a = 6.17 ± 0.04 Å and c = 19.6 ± 0.6 Å. No general or specific extinction conditions were found to limit the possible reflections. There are five space groups of hexagonal symmetry which have no general or special extinction conditions: P622, P6mm, P6m2, P62m and P6/mmm. Of these five, only P6/mmm is centrosymmetric.

Single crystal diffraction measurements of this crystal were done on a computer controlled (program FACS I), four circle, Picker goniometer using Mo Ka radiation and a perpendicular graphite monochromator. Room temperature during the data collection was $22 \pm 3^{\circ}$ C. Preliminary examination confirmed that the crystal has hexagonal symmetry and that it has no general or special extinction conditions. A least squares lattice parameter fit of twelve data points gave the following values: $a = 6.187_9 \pm 0.001_6$ Å and $c = 19.76_4 \pm$ 0.01_5 Å. Table 2 lists pertinent data collection parameters.

Table 2: X-ray Diffraction Data Collection

Mo radiation $\lambda = 0.70926 \text{ Å}$, no filter, kV = 40, ma = 18 ω Scanned $1^{\circ}/\text{min.}$, no attenuator, background time = 20 sec. Perpendicular graphite monochromator, d = 3.354 Å $\sin\theta/\lambda$: 0.03691 Å⁻¹ to 1.15494 Å⁻¹ 662 reflections measured, 107 absent Empirical absorption correction applied V = 655.4 Å³ $\rho(\text{calc}) = 8.3 \text{ g/cc}$ $\mu = 598 \text{ cm}^{-1}$

In correcting the raw data for background radiation, the observed intensity was defined to be zero if the raw intensity was less than two sigma. Sigma, a measure of the uncertainty in the reflection intensity, was calculated from counting statistics by the method of Ibers¹⁴. An empirical absorption correction was applied to the data to reflect the fact that the crystal is not spherical and at different orientations the incident X-ray beam had different path lengths to travel. Strong reflections were chosen and the crystal was rotated full-circle around the angle ϕ in polar coordinates. Rotating a crystal 360° through the X-ray beam, as described, necessarily results in a sinusoidal empirical absorption curve.

The absorption correction was determined after the reflection data had been collected. To achieve a sinusoidal correction the diffractometer had to be realigned. Phi curves around the 120 and the 360 were collected and averaged for the empirical absorption correction.

The raw data set contains two equivalent sets of reflections: the hexagonal symmetry requires that the sets hkl and khl be equivalent because they are related by a mirror plane. Examination of the absorption corrected data shows that the reflections which are supposed to be equivalent do not differ from each other by more than three sigma. These two sets of data were averaged together to give 378 independent reflections.

CHAPTER V

STRUCTURE DETERMINATION

A three dimensional Patterson function was calculated for the data set after the absorption correction had been applied to the data and the equivalent reflections averaged. The centrosymmetric space group P6/mmm was used in the synthesis. Table 3 lists the positions, relative peak heights and assignments to the vectors observed in the map. Table 4 lists the equivalent positions in P6/mmm that describe the vector peak positions.

The largest vector peaks were found in six levels of the Patterson map: fractional w coordinates 0.000, 0.155, 0.187, 0.310, 0.337 and 0.500. These levels were interpreted as being the six distances of separation of planes of metal atoms along the long axis of the unit cell. There are only three types of vector positions in the map: u,0,w; 1/3,2/3,wand 0,0,w. Two image seeking functions¹⁵ were used on the map to establish possible real fragments of the heavy atom positions--(1/3,2/3,z and 2/3,1/3,z) and (0.325,0,z; 0,0.325,zand 0.675,0.675,z). The image seeking functions indicated the 1/3,2/3,z position was real and the x,0,z position was probably real, but for more than one value of x.

The requirement for strong peaks at the level w = 0.187was found to be satisfied by two eclipsed sets of x,0,z positions separated by that increment in z. These positions

P6/mmm Positions	u	v	W	Relative Height	Assignment
la	0.000	0.000	0.000	999	Origin
2c	0.333	0.667	0.000	505	Yb-Yb in same x,y plane
2e	0.000	0.000	0.098	66	Yb(x,0,z)- Anion(x,0,z+ 0.098)
4h	0.333	0.667	0.098	13	Yb(x,0,z)- Anion(0,x,z+ 0.098)
12n	0.325	0.000	0.155	195	Yb(x,0,z)- Yb(1/3,2/3,z+ 0.155)
2e	0.000	0.000	0.187	387	Yb(x,0,z)-Yb (x,0,z)
4h	0.333	0.667	0.187	178	Yb(x,0,z)-Yb (0,x,z)
12n	0.325	0.000	0.255	16	Yb(1/3,2/3,z)- Anion(x,0,z+ 0.255)
12n	0.350	0.000	0.310*	104	Yb(x,0,z)-Yb (x,0,z+0.310)
12n	0.325	0.000	0.337*	195	Yb(x,0,z)-Yb (1/3,2/3,z+0.33)
12n	0.325	0.000	0.405	19	Yb(x,0,z)-Anion (x,0,z+0.405)
1b	0.000	0.000	0.500	171	Yb(1/3,2/3,z)- Yb(1/3,2/3,z+ 0.500)
2d	0.333	0.667	0.500	96	Yb(1/3,2/3,z)- Yb(2/3,1/3,z+ 0.500)
6k	0.350	0.000	0.500	238	Yb(x,0,z)-Yb (x,0,z+0.500)

Table 3:Patterson Map

*Strongly overlapping peaks

Positions	Point Summetry	Coordinates of Equivalent Positions
12n	m	$x,0,z; 0,x,z; \bar{x},\bar{x},z; \bar{x},0,z;$
		0,x,z; x,x,z; x,0,z; 0,x,z;
		$\bar{x}, \bar{x}, \bar{z}; \bar{x}, 0, \bar{z}; 0, \bar{x}, \bar{z}; x, x, \bar{z}.$
6k	mm	$x,0,1/2; 0,x,1/2; \bar{x},\bar{x},1/2;$
		\bar{x} ,0,1/2; 0, \bar{x} ,1/2; x,x,1/2.
4h	3m	1/3,2/3,z; 2/3,1/3,z; 1/3,2/3,z;
		2/3,1/3,z.
2e	6mm	0,0z; 0,0,ž.
2d	ē m2	1/3,2/3,1/2; 2/3,1/3,1/2.
2c	ē m2	1/3,2/3,0; 2/3,1/3,0.
1b	6/mmm	0,0,1/2.
1a	6/mmm	0,0,0.

Table 4: Properties of Space Group P6/mmm¹⁶

disallowed the space group P622 because the only levels possible for x,0,z positions in this symmetry are z = 0 and z = 1/2, a separation of z = 0.500. The space group P6m2 was rejected for the same reason. Space groups P6mm and P6/mmm were not considered because the x,0,z positions in these two symmetries require placing six metal atoms in the same x,y plane. With six metals in the same plane, the best metal-metal separation in x,0,z positions would be 2.06 Å, less than half the Yb-Yb separation found in YbCl₂, for example³.

Of the five possible space groups listed previously, $P\bar{6}2m$ is the only one consistent with the Patterson results.

Table 5 lists some of the equivalent positions of this symmetry, and Figure 1 shows a representation of the symmetry. All the major peaks in the Patterson map are accounted for by placing metal atoms in the positions shown in Table 6. The values of x, y and z for the positions are refined values to be discussed later.

The metal atoms are located in the unit cell in three sets of special positions. Two sets are x,0,z positions around z = 0.000 and z = 0.500 ("staggered" to each other with x = 0.638 and x = 0.369) which account for the Patterson peaks at 0,0,0.187 and 1/3,2/3,0.187--each x,0,z set is split by symmetry into two eclipsed subsets with an average spacing between them of z = 0.187. Between the staggered sets are average distances of z = 0.310 and z = 0.500. The third set of metal atoms occupies the positions 1/3,2/3,z at z = ± 0.251 . Between this third set and the first two are average distances of z equal to 0.155 and 0.337.

Some metal to anion vectors are found in the Patterson map at low peak heights. The x,0,z sets of metal atoms are spaced an average of z = 0.094 above and below the levels of z = 0.000 and z = 0.500. Thus the vector peaks at 0,0,0.098 and 1/3,2/3,0.098 are interpreted to mean that anions are located at the zero and 1/2 levels in positions eclipsed to the surrounding metal atoms. The u,0,w vector positions at w = 0.255 and 0.405 confirm that the anions at the zero and one-half levels are in x,0,z positions in real space.

Positions	Point Symmetry	Coordinates of Equivalent Positions
6i	ш	x,0,z; 0,x,z; x̄,x̄,z; x,0,z̄; 0,x,z̄; x̄,x̄,z̄.
4h	3	1/3,2/3,z; 1/3,2/3,z; 2/3,1/3,z; 2/3,1/3,z.





Atom	x	у	Z	
Anion 1	0.5957	0.0000	0.0000	
Yb 1	0.6383	0.0000	0.0962	
Anion 2	0.5892	0.0000	0.1900	
УЪ 2	0.3333	0.6667	0.2513	
Anion 3	0.3716	0.0000	0.2902	
Anion 4	0.3333	0.6667	0.3578	
ҮЬ З	0.3609	0.0000	0.4073	

Table 6:Refined Atom Positions in Space Group P62m

The arguments outlined above account for the gross spacing and positioning of the vector peaks in the Patterson However, the peak heights and shapes proved difficult map. to completely predict in an a priori manner from the proposed To prove that this model is consistent with the model. observed Patterson map, two new Patterson maps were calculated--one for the refined metal atom positions alone and one for the metal and anion positions listed in Table 6. The results of these two maps are listed in Table 7. Even though the final refinement must be regarded as only tentative (for reasons to be discussed later), the Patterson syntheses from calculated structure factors show close agreement with the vector map derived from the observed reflection data. Even the three dimensional shapes are reproduced closely.

u	v	W	Rel Metals	ative Heights Metals and Anions
0.000	0.000	0.000	999	999
0.333	0.667	0.000	485	495
0.000	0.000	0.099	0	69
0.333	0.667	0.099	0	27
0.325	0.000	0.155	196	190
0.000	0.000	0.189	380	377
0.333	0.667	0.189	178	175
0.325	0.000	0.255	0	19
0.350	0.000	0.310	100	100
0.325	0.000	0.337	201	200
0.350	0.000	0.405	0	19
0.000	0.000	0.500	173	173
0.333	0.667	0.500	112	102
0.350	0.000	0.500	240	240
	u 0.000 0.333 0.000 0.333 0.325 0.000 0.333 0.325 0.350 0.350 0.000 0.333 0.350	u v 0.000 0.000 0.333 0.667 0.000 0.000 0.333 0.667 0.325 0.000 0.333 0.667 0.325 0.000 0.333 0.667 0.325 0.000 0.350 0.000 0.350 0.000 0.350 0.000 0.350 0.000 0.333 0.667 0.350 0.000	uvw0.0000.0000.0000.3330.6670.0000.0000.0000.0990.3330.6670.0990.3250.0000.1550.0000.0000.1890.3330.6670.1890.3250.0000.2550.3500.0000.3100.3250.0000.3370.3500.0000.4050.0000.0000.5000.3330.6670.5000.3500.0000.500	uvwRel Metals0.0000.0000.0009990.3330.6670.0004850.0000.0000.09900.3330.6670.09900.3250.0000.1551960.0000.0000.1893800.3330.6670.1891780.3250.0000.25500.3500.0000.3372010.3500.0000.40500.3330.6670.5001730.3330.6670.5001120.3500.0000.500240

Table 7: Patterson Maps from Final Refinement

*Strongly overlapping peaks

The final least squares refinement of the atomic positions listed in Table 6 and the corresponding temperature factors listed in Table 8 contains only those positions which were statistically stable. After eight cycles of refinement, the largest shift in a metal position parameter was 0.00009 and for the anion position parameters 0.0007. The largest shift in the anisotropic metal B values was 0.05 and for the isotropic anion B values 0.02.

Atom	B11 or B	B22	B33	B12	B13	B23
Anion 1	-2.44					
ҮЬ 1	-1.53	-0.81	0.65	-0.81	-0.02	0.00
Anion 2	-1.74					
ҰЪ 2	-1.00	-1.00	1.34	-1.00	0.00	0.00
Anion 3	4.96					
Anion 4	0.23					
ΥЪ 3	-1.20	-1.27	1.56	-1.27	0.21	0.00

Table 8. Temperature Factors

Scattering factor tables and a correction for anomalous dispersion were included in the least squares refinement. The scattering factors computed by Cromer and Waber¹⁷ were used for the ytterbium and chloride ions, those of Tokonami¹⁸ were used for the oxide ion. The anomalous dispersion corrections of Cromer¹⁹ were used. The scattering factor tables allow corrections for an atom interacting with the incident X-ray beam as a function of the scattering angle. Anomalous dispersion is an effect by which an atom that is absorbing radiation strongly will scatter radiation with different phase changes than the other atoms in the structure.

With only the metal atoms in the refinement and with isotropic temperature factors, an R value of 0.196 was attained. Employing anisotropic motion gave an R value of 0.136 for the metal atoms alone. For the final refined parameters listed in Table 6 and Table 8, an R value of 0.101 was achieved.

Fourier and difference Fourier series were computed at several stages in the refinement. With only the metal atom positions occupied, both the Fourier and the difference Fourier showed light atoms located directly above and below the metal atom positions, in agreement with observed Patterson peaks. Additionally, the difference map showed that light atoms should be put in the same x,y planes as the x,0,z metal atoms. The Fourier showed no peaks in these positions.

Of the light atom positions indicated by the difference Fourier, only the four listed in Table 6 could be refined simultaneously with the metal atoms. This problem will be addressed later. A Fourier and difference Fourier were computed from the final refinement. The Fourier only shows electron density at the seven refined atomic positions. A structure factor table is included as Appendix I. The difference map is not flat--large peaks are again evident in the same x,y plane as the x,0,z metal positions. Otherwise, no peaks are seen in the difference Fourier.

The remaining cyrstals of the same morphology as the one that has been investigated above were collected for X-ray fluorescence and powder diffraction experiments. The powder pattern, although weak because of the small amount of sample present, was indexed successfully on the hexagonal unit cell and lattice parameters found for the single

crystal. This result is tabulated as Appendix II. Included with the pattern are both the observed intensities and relative intensities for the corresponding single crystal reflections.

The X-ray fluorescence experiment was run on the powder sample to confirm the presence of ytterbium. For reasons to be discussed later, an investigation for tantalum was included in the analysis. The $L\alpha_1$ peaks of both metals were to be observed. At high gain a small but definite ytterbium peak was seen, but the presence of tantalum could neither be confirmed nor denied because of interference from platinum and copper. Of the three materials available as sample holders, platinum interfered strongly with the tantalum peak, aluminum contained too much interfering copper impurity and at the high gains necessary to observe an ytterbium response, quartz impurities interfered also. Peaks in the fluorescence spectra of both platinum and copper give strong responses at the scattering angle of the tantalum La_1 peak.

CHAPTER VI

DISCUSSION

After the metal atom positions of the unit cell had been determined, it was seen that the phase being investigated contained atoms other than just ytterbium and chlorine. From a consideration of the closest packing of hard spheres with radii equal to the crystal radius of the chloride anion $(1.81 \text{ Å})^{20}$, calculations show that between six and seven layers of three chloride ions each can be packed within the dimensions of the unit cell. Allowance for negative deviations from this crystal radius allows for up to eight or nine layers, or a maximum of 27 negative charges in the unit cell. Even the assumption that all 16 metal positions are filled by divalent ytterbium leaves a deficiency of five negative charges.

This problem may be solved by recognizing oxygen as a likely contaminant. Ytterbium oxide chloride is known¹ to form in ytterbium chloride systems when a trace of water is present. From a single crystal structural study²¹ the following lattice parameters are reported for hexagonal YbOC1: a = 3.726 Å, c = 27.830 Å. The atomic positions of YbOC1 all lie on the z-axis of the unit cell, forming linear anionmetal-anion interactions. The Patterson and Fourier maps in this study indicate linear anion-metal-anion interactions, parallel to the z-axis of the unit cell. An oxide anion has

a much smaller crystal radius $(1.40 \text{ Å})^{20}$ than does the chloride anion. The double negative charge on the oxide anion also requires that fewer of these anions be put in the unit cell. However, a combination of space group symmetry and closest packing considerations still restricts to three the number of oxide anions that can be placed in any x,y plane.

The final refinement listed in Table 6 and Table 8 identifies four anion positions. Anions 1, 2 and 4 were assigned the oxide anion scattering factor table during the least squares refinement; Anion 3 was assigned the chloride anion scattering table. This assignment was made in earlier cycles of refinement; with more than four anion positions occupied, Anion 3 had metal-anion distances closer to those of Yb-Cl than Yb-O (see below). With just four anion positions occupied, the metal-anion distances of separation have readjusted to different values, so no definite identification of the anions should be made from metal-anion separation distances until after the structure has been completed.

In Table 9 some selected interatomic distances for the refined atomic positions are listed. These distances represent the closest approach between layers of atoms and were obtained from a complete computation of all distances less than five angstroms. Table 10 lists angles between several sets of atoms.

From Table 9 it can be seen that the anion to metal distances of separation are no greater than 2.3 $\stackrel{\circ}{A}$. These

Atoms	Distance	Estimated Standard Deviation
Anion 1 to Anion 1	3.259 Å	0.003 Å
Yb 1 to Yb 1	3.431	0.001
Anion 2 to Anion 2	3.238	0.002
Yb 2 to Yb 2	3.573	0.001
Anion 3 to Anion 3	3.386	0.003
Anion 4 to Anion 4	3.573	0.001
Yb 3 to Yb 3	3.434	0.001
Yb 1 to Anion 1	1.920	0.002
Yb 1 to Anion 2	1.878	0.002
Yb 1 to Yb 2	3.650	0.002
Yb 2 to Anion 2	2.228	0.001
Yb 2 to Anion 3	2.100	0.002
Yb 2 to Anion 4	2.104	0.005
Yb 2 to Yb 3	3.666	0.002
Yb 3 to Anion 3	2.316	0.002
Yb 3 to Anion 4	2.212	0.002
Anion 1 to Anion 2	3.755	0.003
Anion 2 to Anion 3	2.394	0.003
Anion 2 to Anion 4	3.806	0.005
Anion 3 to Anion 4	2.368	0.003

Table 9:Interatomic Distances

distances are shorter than the ytterbium to chloride distance in YbOCl $(2.75 \text{ Å})^{21}$ or in YbCl₂ $(2.76 \text{ Å})^3$. They are comparable to the ytterbium to oxygen distance in YbOCl $(2.2 \text{ Å})^{21}$. It appears then that the distances calculated from the atomic positions of the final refinement support oxide anions in the refinement rather than chloride anions.

Angle	Degrees	Estimated Standard Deviation
Yb 1 - Anion 1 - Yb 1	164.2 ₁ °	0.2 ₇ °
Anion 1 - Yb 1 - Anion 2	162.8 ₀	0.16
Anion 2 - Yb 2 - Anion 3	67.10	0.07
Anion 2 - Yb 2 - Anion 4	122.95	0.03
Anion 4 - Yb 3 - Anion 3	63.0 ₁	0.12
Yb 1 - Anion 2 - Yb 2	125.23	0.03
Yb 2 - Anion 4 - Yb 3	103.09	0.06
Yb 2 - Anion 3 - Yb 3	99.36	0.06

Table 10: Interatomic Angles

Final assignment of anion positions may not be made because the structure is too incomplete--anion positions could not be refined at the z = 1/2 level. Chemically, anions must occupy this vacant level and are required to balance the positive charges of the surrounding metal atoms. As stated previously, the Patterson vectors indicate only anions eclipsed to the metal atoms at this level. Additionally, the difference Fourier calculated with only the metal positions occupied indicates a similar result. In all refinements, however, the least squares program was unable to find a statistical minimum for the atomic parameters at this level. Setting the temperature factor to a constant value for anion positions at the z = 1/2 level did not allow the position parameters to refine; populating the special positions 1/3, 2/3, 1/2 and 0, 0, 1/2 did not help either. Difference Fouriers calculated with other anion positions occupied did not even show a small peak at the z = 1/2 level.

There are several possible explanations for this inability of the entire structure to refine. Some of these include a bad crystal or data set, a bad absorption correction, the wrong space group or even the wrong assumptions about the chemistry of the reaction that formed the crystal.

Although very small, the crystal gave good sharp reflections with the 00l reflections found to have a mosaic spread of 0.5° during a 20 scan. This spread is indicative that there was not a large amount of disorder in the crystal. Some bad reflections may be in the data set, though. In the course of refinement it was noted that the calculated structure factor for a strong 006 reflection was twice the observed value. When this reflection was deleted from the data set, the R value dropped considerably and a few additional anion positions could be located. The 006 reflection was the only strong reflection to stand out in this manner, and it was the only one deleted from the data set. The complete list of observed and calculated structure factors is given in Appendix I.

Table 2 lists a very large linear absorption coefficient (598 cm^{-1}) for the crystal being investigated. As described earlier, the empirical absorption measured small angular variations in the intensity of a reflection. For crystals that absorb X-rays strongly, the empirical correction measures small variations in a large absorption effect, allowing the correction to be imprecise.

As mentioned previously, P62m is the only space group of the five groups considered which could accommodate the metal orientation that was consistent with the Patterson map. Yet there is a very special type of crystal twinning that could be operating in this system--Buerger²² warns that in apparently hexagonal cells which have no general or special extinction conditions, the possibility of trilling should be considered. Trilling is a twinning mechanism by which three orthorhombic cells of symmetry 2mm are intergrown in a manner that yields an additional mirror plane for a combined symmetry as high as 6/mmm. Intergrowth such as this masks the true extinction conditions.

The observation of pseudo-extinctions or periodic arrangements of weak reflections might support this or other twinning mechanisms. A pseudo-extinction is especially noticeable along the 00l axis where the intensity for a reflection with an even numbered l is consistently greater than for an odd numbered l. In defense of the solution, however, it should be pointed out that the least square refinement and calculated structure factors match this odd-even behavior quite closely.

The assumption that ytterbium was the only heavy atom in the crystal was also investigated. The crystal was isolated from a reaction carried out in a sealed tantalum ampoule, so tantalum is a possible heavy metal contaminant. Additionally, the possibility of tantalum being present in the crystal was investigated because of certain similarities between published structures in a tantalum oxide system^{23,24} and results of this study. Specific points of similarity are some tantalum oxygen distances of less than 2.0 $\overset{\mathrm{o}}{\mathrm{A}}$ and negative temperature factors for some of the metal atoms and anions. In the tantalum contamination model of the structure being investigated in this work, the two x,0,z sets of metal positions can be interpreted as groups of composition Ta_60_{15} , with nine oxygen atoms above, below and bridging the x,0,z metals. Six oxygen atoms occupy positions previously mentioned as being large peaks in the difference Fourier calculated from metal occupancy only: anion positions almost in the same plane as the metal atoms, in x, 0, zpositions staggered to the metal positions.

This tantalum contamination theory is rejected. One reason is that the oxide anion position in the same planes as the x,0,z metal positions cannot be refined, the least squares program being unable to find a position for it. Additionally, this oxide anion position gives a closest oxygen-oxygen approach of less than the sums of the two crystal radii.

The peak in the difference map that gave rise to the tantalum oxide impurity speculation is not attributed to a real anion position but rather to a reflection of the anisotropic motion of the nearby metal atom. The short ytterbiumoxygen anion distances listed in Table 9 and the negative temperature factors in the final refinement are attributed to a lack of electrons in the refinement--*i.e.*, an incomplete structure. Small changes in the position coordinates of the atoms in a complete refinement could add 0.2 $\stackrel{\circ}{A}$ to the short distances. The negative temperature factors are a result of the least squares program trying to match the observed structure factors. If more electrons could be included in the refinement, the temperature factor would not have to be varied so much to calculate good structure factors.

The results of this crystal study can be tied to other work with lanthanide series elements. Caro has reported a study²⁵ of the crystal structures of rare-earth oxides and oxide salts and is able to describe these structures as OM_4 tetrahedra sharing edges. Specifically, the structure of an oxide chloride is described in this theory as sheets of OM_4 tetrahedra, each sharing four edges.

Caro's theory is consistent with only part of the structure found in this study. Tetrahedral orientation for the metal atoms cannot exist for the x,0,z positions at z =0.096 and z = 0.407. Each of these sets of metal atoms is eclipsed by symmetry, so oxygens at z = 0 and z = 1/2 do not conform to Caro's theory. Tetrahedral orientation does

exist between x,0,z and the 1/3,2/3,z metal positions which are staggered to each other. Anions located in planes between these metal positions must necessarily be located in a tetrahedral M₄ net although the last three angles listed in Table 10 show large deviations from the 109° angles of a regular tetrahedron.

Fishel² attempted to prepare crystals of Yb_30_4Cl analogous to the phase $Y_30_4Cl^{26}$. From his work a new phase of unknown composition resulted. A comparison of the X-ray powder diffraction pattern listed in Appendix II to that reported by Fishel shows no relationship between these two phases.

CHAPTER VII

CONCLUSION

The intent of this research was to characterize a mixed oxidation state in the ytterbium(II)-ytterbium(III) chloride system. Based on ionic size considerations and observed metal-anion distances from the partial structure refinement that was possible, the phase probably contains oxygen atoms.

Sixteen ytterbium atoms are contained in the unit cell in two types of special positions: two sixfold x,0,z positions and a fourfold 1/3,2/3,z position. Moreover, anions occupy only these two types of positions as indicated by the Patterson map, Fouriers and difference Fouriers, and the partial refinement of three metal and four anion positions. As a necessary consequence of space group P62m, these sets of ions are located in a layered pattern along the long c-axis of the unit cell, in good agreement with the plate-like morphology of the phase.

The ytterbium positions and the partial set of refined anion positions may be interpreted in terms of three possible models for the complete crystal structure. All three models assign both x,0,z sets of metal atoms to Yb_20_3 structural units. The first model consists of the 1/3,2/3,z metal atoms as part of linear units of YbCl₂, the second puts YbOCl units in these positions, and the third has YbO units in the fourfold position.

These three models require a linear group around the fourfold position. Of the three possibilities, YbO units must be linear, units of YbOC1 are reported²¹ to be linear, and units of YbC1₂ are reported³ to have a bent configuration. Because the oxide chloride is a known¹ contaminant in ytterbium chloride systems, the model chosen for the complete structure is the one having YbOC1 units in the fourfold positions. The final structure by this model would consist of sesquioxide and oxide chloride units to build the Yb₁₆0₂₂Cl₄ unit cell, or (Yb₂0₃)₆(YbOC1)₄. This formula was used to calculate a density and linear absorption coefficient for the crystal, as listed in Table 2.

Figures 2-4 show three projections of this structural model. Figure 2 is a projection of the refined metal atom positions on the (001) plane, Figure 3 is a projection of the refined anion positions on the (001) plane. Numbering of positions on both figures corresponds to the numbering system of the final refinement (Table 6). Figure 4 is a projection of the $Yb_{16}0_{22}Cl_4$ model on the (010) plane. The darker circles of Figure 4 represent atomic positions in the (010) plane, the fully dashed circles represent anion positions that are not refineable. Figure 3 shows the near-eclipsing of x,0,z anion positions, Figure 4 shows the layered packing of ions in the unit cell.

The unit cell for the above model may be considered to be derived from the hexagonal symmetry of YbOC1 with that of the cubic symmetry exhibited in ytterbium sesquioxide.



Figure 2: Projection of Metal Atom Positions on (001) Plane



Figure 3: Projection of Anion Positions on (001) Plane.



Figure 4: Projection of $Yb_{16}0_{22}Cl_4$ on (010) Plane.

Wyckoff²⁷ indicates that the sesquioxide unit cell contains 16 sesquioxide units; the metal atoms are in special positions at four levels on the z-axis, with 24 atoms in an x,0,z closest packing type of position in the Ia3 space group and eight in special positions at $z = \pm 1/4$. The oxygen atoms are in the 48 general positions. Substitution of chloride ions for some of the oxygen atoms in the cubic sesquioxide lattice probably distorts the symmetry to hexagonal because the large chloride ion increases the anion to cation radius ratio. The structure remains similar, the symmetry changes.

The structure is not refineable further than the metal positions and four anion positions, most likely the result of a faulty data set or a bad absorption correction. Possibly a few strong reflections were measured at an intensity less than the actual value. This condition would be similar to that mentioned earlier in which the 006 reflection had to be deleted from the data set. Reasons for the reflections being recorded at too low intensity values are not known but probably reflect an absorption or extinction problem. As discussed earlier, for a small crystal that absorbs X-rays strongly, a good absorption correction may be difficult to obtain.

The possibility of twinning cannot be completely rejected until the crystal structure is solved: the probability of twinning is lessened by the sharp diffraction peaks

observed in the data set. A twinning geometry would have to be of a precise nature that did not introduce disorder into the crystal and broaden the diffraction peaks.

The final solution will require at least the collection of another data set--hopefully from a larger crystal which is not now available. Since the full structure is not known, a direct reaction to obtain more of this phase may not be possible. A repetition of the one reaction which led to this phase may reproduce the conditions which led to its accidental formation.

The original intent of this research was to increase an understanding of the structural aspects of phases of intermediate oxidation states in the ytterbium(II)-ytterbium(III) chloride system. The new phase that was isolated was contaminated by oxygen and only a partial structure could be obtained. This result may not help characterize the chloride system, but it does help characterize the reactions used to obtain the phases in the chloride system. The phase that was isolated as a side product of these reactions and its presence can now be rapidly identified from the X-ray powder diffraction pattern. REFERENCES

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APPENDICES

APPENDIX I: Structure Factor Table

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100	5.3589 Å	5.3535 Å	vw	25
111	3.0567	3.0450	m	54
112	2.9526	2.9377	m	41
113	2.8005	2.7965	vw	16
114	2.6223	2.6212	vw	47
202	2.5861	2.5781	vw	17
115	2.4364	2.4309	w	47
211	2.0149	2.0099	vw	22
300	1.7863	1.7811	m	88
306	1.5703	1.5672	vw	69
221	1.5423	1.5357	vw	50

APPENDIX II: Observed and Calculated Powder Pattern

*Indexing based on a = 6.1879, c = 19.7637 \mathring{A}