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The Hydrothermal Preparation, Single-Crystal Lattice Parameters, and Decomposition Data for Some Lanthanide Dihydroxy Chlorides and the Related Hydroxy Chloride, $Yb_3O(OH)_5Cl_2$

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The dihydroxy chlorides of La, Nd, Sm, Gd, and Y and the related compound $Yb_3O(OH)_5Cl_2$ have been prepared hydrothermally at 500°. The compounds $La(OH)_2Cl$, $Nd(OH)_2Cl$, $Sm(OH)_2Cl$, and $Gd(OH)_2Cl$ form an isomorphous series whose monoclinic lattice parameters have been determined by single-crystal techniques and fitted to quadratic equations by the method of least squares. Accurate lattice parameters for the orthorhombic form of $Y(OH)_2Cl$, prepared previously, and the orthorhombic $Yb_3O(OH)_5Cl_2$ also have been determined. The monoclinic rare earth dihydroxy chlorides decompose thermally under nitrogen to form the oxychlorides and water. Approximate heats of decomposition have been determined. $Yb_3O(OH)_5Cl_2$ decomposed to the sesquioxide and $Y(OH)_2Cl$ to a mixture of the oxychloride and sesquioxide.

Introduction

In the course of preparing yttrium–iron garnet single crystals under varying hydrothermal conditions two different crystalline forms of yttrium dihydroxy chloride, $Y(OH)_2Cl$, and a related hydroxy chloride $Y_3O(OH)_5Cl_2$ have been isolated by Klevtsov, Klevtsova, and their coworkers.[1–4] In an attempted hydrothermal preparation of lanthanum aluminate at 500° from La_2O_3 and $AlCl_3 \cdot 6H_2O$ in a 15% NH_4Cl solution S. L. obtained the first known crystalline rare earth dihydroxy chloride, $La(OH)_2Cl$[5] (in addition to α-Al_2O_3). In view of considerable current interest in the electromagnetic properties of single crystals containing the rare earth elements, it appeared desirable to characterize some of the rare earth analogs of the yttrium hydroxy chlorides. Data on the preparation, lattice parameters, and thermal decomposition of the monoclinic crystals of $La(OH)_2Cl$, $Nd(OH)_2Cl$, $Sm(OH)_2Cl$, and $Gd(OH)_2Cl$ are given here in addition to similar information for the orthorhombic form of $Y(OH)_2Cl$ and for $Yb_3O(OH)_5Cl_2$.

An additional, and, in the long range, more compelling reason for the study of these materials is that such isomorphous series of rare earth compounds represent ideal grounds for testing theories of transition metal covalent bond formation (among other theories) as a function of d character and size. Structural determinations[2–4,6] have shown that the four compounds $Y(OH)_2Cl$ (orthorhombic), $Y(OH)_2Cl$ (monoclinic), $Y_3O(OH)_5Cl_2$, and $La(OH)_2Cl$ are closely related[7] layer type of structures where the layers are held together by predominantly $O-H \cdots Cl$ hydrogen bonds. This suggests that a short bond distance obtained in such materials is likely to be a more valuable representation of an unstrained bond than in a simpler compound like LaOCl with three-dimensional arrays of strong bonds. While the structures of the yttrium compounds have all been reported as being centrosymmetric,[2–4] the lanthanum dihydroxy chloride is noncentrosymmetric.[6] This suggests that these lanthanide compounds are not only suitable candidates for ferroelectric, magnetoelectric, and other similar studies, but also, in consideration of their layer structure, candidates for the testing of theories of magnetic cluster formation.

Experimental Section

Materials.—Reagent grade NH_4Cl, $AlCl_3 \cdot 6H_2O$, HNO_3, and HCl were used. The rare earth oxides, all 99.9% pure with respect to the lanthanides, were from American Potash (La_2O_3, Sm_2O_3, Gd_2O_3, and Y_2O_3), Research Chemicals (Nd_2O_3), and Michigan Chemical (Yb_2O_3).

Hydrothermal Preparations.—The vessels used in the preparations listed in Table I were of two types. One described by May, *et al.*,[8] consisting of a platinum liner in a nichrome carrier, was found to be operable at 20,000 psi and 550°. The second type was similar to that described by Tuttle and Friedman[9] but with a gold liner and a single 2-in. No. 12 thread. After loading and closure, the vessel was heated in a cylindrical furnace at 500 ± 3° and maintained for 2–5 days at temperature.

X-Ray Data.—The new single-crystal lattice parameter data presented in Table II were manually collected on a carefully aligned Picker Nuclear four-circle goniostat using Mo Kα radiation (λ_{α_1} 0.70926 Å). All crystalline specimens used had a maximum dimension no larger than 110 μ and were mounted on specially stable arcless goniometer heads.[10] The crystals were visually perfect and gave sharp (exception—$Y(OH)_2Cl$), smooth peaks at high 2θ (narrow slit width, slow scan). The 2θ peak positions were determined using quarter-peak intensity heights (half for $Y(OH)_2Cl$) of the Kα_1 line. For each specimen χ, φ, ω, and 2θ (>62°) were measured to a precision of 0.01° for more than 30 reflections. The errors listed in Table II are estimated from a comparison of lattice parameters for different crystals of the same composition and probably include the effects

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(1) P. V. Klevtsov, R. F. Klevtsova, and L. P. Sheina, *Zh. Strukt. Khim.*, **6**, 469 (1965).

(2) R. F. Klevtsova and P. V. Klevtsov, *Dokl. Akad. Nauk SSSR*, **162**, 1049 (1965).

(3) R. F. Klevtsova and P. V. Klevtsov, *Zh. Strukt. Khim.*, **7**, 556 (1966).

(4) R. F. Klevtsova, L. P. Kozeeva, and P. V. Klevtsov, *Izv. Akad. Nauk SSSR, Neorgan. Materialy*, **3**, 1430 (1967).

(5) N. V. Aksel'rud and V. B. Spivakovskii (*Zh. Neorgan. Khim*, **5**, 327, (1960)) have described the formation of presumably amorphous $La(OH)_2Cl$ by the addition of NaOH solution to one containing $LaCl_3$. They established the composition of the precipitate by a potentiometric method.

(6) See a preliminary account of the structure by F. L. Carter, Proceedings of the Sixth Rare Earth Conference, May 3–5, 1967, Gatlinburg, Tenn., 1967, p 187. The completed structure will be submitted for publication in the near future.

(7) K. Dornberger-Schiff and R. F. Klevtsova, *Acta Cryst.*, **22**, 435 (1967).

(8) I. May, J. J. Rowe, and R. Letner, U. S. Geological Survey Professional Paper 525-B, Geological Survey Research, 1965, p 165.

(9) O. F. Tuttle and I. I. Friedman, *J. Am. Chem. Soc.*, **70**, 919 (1948).

(10) F. L. Carter and W. C. Sadler, *J. Appl. Cryst.*, **2**, 145 (1969).

TABLE I

HYDROTHERMAL PREPARATION OF DIHYDROXY CHLORIDES AT 500 ± 3°[a]

Run	Reagents	Quantity	Final pH	Products and comments
1	La_2O_3 $AlCl_3 \cdot 6H_2O$ 15% NH_4Cl soln	0.001 mol 0.002 mol 1.5 ml	<7	a. α-Al_2O_3 b. $La(OH)_2$ crystals, acicular, 1–3 mm long
2	La_2O_3 1 *N* HCl soln 15% NH_4Cl soln	0.0005 mol 1.0 ml 0.5 ml	<7	$La(OH)_2Cl$ crystals, acicular, 1–2 mm long
3	La_2O_3 1 *N* HCl soln	0.00075 mol 1.5 ml	6–7	$La(OH)_2Cl$ crystals, acicular, yield >80%
4	La_2O_3 15% NH_4Cl	0.003 mol 4.5 ml	~9	$La(OH)_2Cl$ crystals, coarse, acicular, to 5 mm long
5	Nd_2O_3 15% NH_4Cl	0.003 mol 4.5	~9	$Nd(OH)_2Cl$, crystals, blue, coarse, acicular, and long plates to 5 mm
6	Sm_2O_3 15% NH_4Cl	0.003 mol 4.5 ml	~9	a. $Sm(OH)_2Cl$, crystals, and yellow, fine, long needles to 2 mm b. $Sm(OH)_2Cl$, yellow, crystalline, fine needle mass
7	Gd_2O_3 15% NH_4Cl	0.003 mol 4.5 ml	~9	$Gd(OH)_2Cl$, crystals, predominantly needles to 2 mm, fine needle mass
8	Yb_2O_3 15% NH_4Cl	0.003 mol 4.5 ml	~9	a. $Yb_3O(OH)_5Cl_2$, crystals, fine needle mass, plus unknown b. $Yb_3O(OH)_5Cl_2$ crystals, long, very thin, rectangular platelets to 3 mm
9	Y_2O_3 15% NH_4Cl	0.003 mol 4.5 ml	~9	a. $Y(OH)_2Cl$, powder composed of orthorhombic modifications, cloudy, easily cleaved crystallites b. $Y(OH)_2Cl$, long, thin, clear platelets to 4 mm

[a] Reaction vessel[8] with 37% fill was used in runs 1–3 and a different vessel[9] with 25% fill was used in the remainder. Runs held at temperature for 4 days (run 1), 5 days (run 2), or 2 days (runs 3–9).

TABLE II

SINGLE-CRYSTAL LATTICE PARAMETERS

Compd	Temp range, °C	*a*, Å	*b*, Å	*c*, Å	β, deg	Vol, Å^3	Lattice[a]
$La(OH)_2Cl$	21.4–22.2	6.3246 (5)[e]	3.9922 (5)	6.9340 (5)	113.900 (10)	160.1	M
$Nd(OH)_2Cl$	23.0–25.0	6.2144 (5)	3.8765 (5)	6.8237 (5)	113.187 (10)	151.1	M
$Sm(OH)_2Cl$	19.8–22.2	6.1838 (5)	3.8121 (5)	6.7559 (5)	112.301 (10)	147.3	M
$Gd(OH)_2Cl$	22.0–25.0	6.1647 (5)	3.7490 (5)	6.7153 (10)	111.271 (10)	144.6	M
$Y(OH)_2Cl$[b]		6.14[f]	3.62	6.60	107	140.3	M
$Y(OH)_2Cl$	22.0–25.1	6.244 (4)	12.645 (6)	3.605 (2)		284.6	O
$Y(OH)_2Cl$[c]		6.21 (3)	12.56 (6)	3.62 (2)		282.4	O
$Yb_3O(OH)_5Cl_2$	25.6–27.7	8.2407 (5)	13.1080 (5)	3.6098 (5)		389.9	O
$Y_3O(OH)_5Cl_2$[d]		8.24[f]	13.23	3.73		406.6	O

[a] M and O refer to monoclinic and orthorhombic lattices, respectively. [b] Reference 3. [c] References 1 and 2. [d] Reference 4. [e] Estimated errors are given in parentheses. [f] Estimated error not known.

of small systematic errors related to the crystal centering, goniostat machining tolerances, etc. These listed errors are at least five times greater than the standard deviations computed[11] from the least-squares statistics. The temperature range listed is that of the air enclosed with the goniostat by a dust shield and presumed to be that of the crystal. Prior to the collection of data on the goniostat, all single crystals were examined for crystal quality and systematic absences *via* film techniques using a Buerger precession camera (Mo Kα radiation). Powder photographs were used primarily for general identification purposes and were taken with a 114.6-mm diameter Philips camera. The films were measured with a Grant Instruments, Inc. comparator which gives a reproducibility of ±2 μ.

Thermal Analysis.—The decomposition data for the hydroxy chlorides were obtained using a Perkin-Elmer differential scanning calorimeter, Model 1-B, with hand-picked samples pressure-sealed in aluminum pans. Just prior to use, the lids of the sample pans were punctured to release the expected gaseous decomposition products. The data were collected with the rate of temperature increase equal to 20°/min, and calibration of the thermal scale of the calorimeter was accomplished using a known weight of indium, whose heat of fusion was taken to be 64.0 mcal/mg. Simultaneous gas effluent analysis was also employed using nitrogen (30 cm^3/min) as a carrier and a built-in thermal conductivity detection system. Sample weights (generally 5–10 mg) and weight changes were determined on a Mettler M-5 microbalance. All strip chart areas were measured with a compensating polar planimeter.

Visual observations of the decomposition of $La(OH)_2Cl$ were made with a temperature rate of increase of 2°/min using a shielded nichrome-wound Vycor tube furnace and a Bausch and Lomb stereoscopic microscope. Well-defined clear colorless crystals of $La(OH)_2Cl$ turned opaque white in the temperature range of 408–411° but retained their shape without evidence of crumbling.

Chemical Analysis.—Although gravimetric analysis of the hydrothermal products was prevented by the low total yields, the following evidence supports the compositions of the formulas as given in the tables. (1) A positive test for Cl using $AgNO_3$ was obtained when the crystals were dissolved in concentrated nitric acid solution. (2) The microscopic chloroplatinate test for NH_3 was negative for crystals grown in NH_4Cl solutions. (3) Spectroscopic analysis of the crystals showed that only the designated rare earth metal (or yttrium) was present in greater than trace amounts. (4) Mass spectrographic analysis of the gaseous-decomposition product of $La(OH)_2Cl$ showed no peaks corresponding to Cl or La at any time but did show increased peaks for masses 17 (OH) and 18 (H_2O) as the product was heated from liquid N_2 temperature to approximately 500° where gas evolution ceased. Fractions of the gas evolved at different temperatures were analyzed on a Consolidated Electrodynamics Corp. instrument. (5) Weight losses associated with decomposition are in reasonable agreement with the theoretical expectation for the materials that decompose to a single product (exception $Y(OH)_2Cl$). (6) Identification of the oxychloride solid decomposition products of the rare earth monoclinic dihydroxy chlorides was accomplished using X-ray powder techniques and these agreed within ±0.0007 Å of those *d* values given by the ASTM card file. Yttrium dihydroxy chloride decomposed to give both YOCl and poorly formed Y_2O_3 at 500° but oxidized to give only Y_2O_3 when heated at 600° for 3 hr. The ytterbium hydroxide chloride, $Yb_3O(OH)_5Cl_2$, decomposed into the sesquioxide. (7) The composition of $La(OH)_2Cl$ has been confirmed by X-ray single-crystal structural analysis[6] as has the composition of the compounds $Y(OH)_2Cl$ (monoclinic), $Y(OH)_2Cl$ (orthorhombic), and $Y_3O(OH)_5Cl_2$.[2–4] A consideration of the similarities of the lattice parameters between these better established compounds and the others of Table II leaves little doubt as to the composition of the remaining members. (8) Finally, semiquantitative results of X-ray fluorescence analysis for the metal content of three small samples including $La(OH)_2Cl$, $Nd(OH)_2Cl$, and $Gd(OH)_2Cl$

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(11) The ALGOL least-squares program used is a modified version of one supplied by Dr. K. Knox.

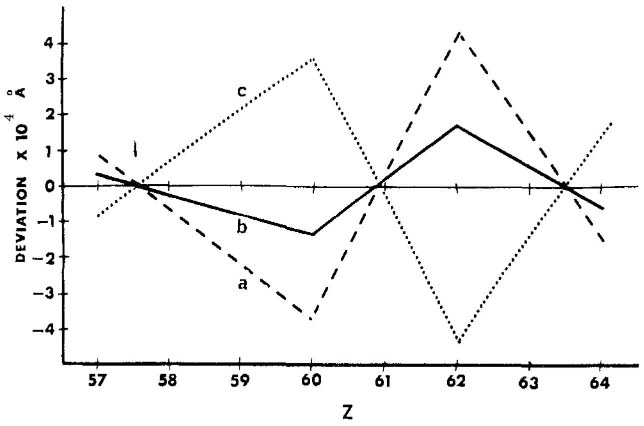

Figure 1.—The deviations of the least-squares calculated values of the unit cell edges from the measured values are given as a function of atomic number. The coefficients of the parabolic fit are given in Table III. The corresponding deviations for the β angle are similar to curve c if multiplied by a factor of 10 (in degrees).

agreed roughly (within 25 wt %) with the calculated expected value. The remaining compounds were either too severely contaminated with debris resulting from opening the bomb or were not available in sufficient quantity for even X-ray fluorescence analysis.

Discussion and Results

All the hydrothermal preparations reported in Table I yielded hydroxy chloride crystals which were transparent, were insoluble in water, did not readily dissolve in 6 *N* hydrochloric acid at room temperature, but did dissolve in concentrated hydrochloric acid or nitric acid upon heating. The various $La(OH)_2Cl$ preparations gave indistinguishable X-ray powder photographs and obviously formed an isomorphous series with $Nd(OH)_2Cl$, $Sm(OH)_2Cl$, and $Gd(OH)_2Cl$. The hydrothermal preparation using Yb_2O_3 (Table I, run 8) yielded a mass of needles plus $Yb_3O(OH)_5Cl_2$ platelets, the latter identified primarily by the similarity of their single-crystal data to those of $Y_3O(OH)_5Cl_2$. Comparison of the X-ray powder photographs of the needles with a powdered platelet indicated an additional product. In an effort to identify the unknown material, numerous specimens were examined by single-crystal precession techniques. Most of these proved to be either clear blades or (in contrast) translucent opalescent needles of $Yb_3O(OH)_5Cl_2$. In addition approximately 0.01% of the crystalline mass was found to be the orthorhombic form of $Y(OH)_2Cl$. These occurred as small crystals ($\sim 60 \times 40 \times 30\ \mu$) and were identified by their appearance (thick, approximately hexagonal platelets, often cloudy, and easily cleaved), by lattice parameters, and by metal X-ray fluorescence analysis. The additional component in the powder pattern, constituting about 10–20% of the mass of needles, remains unidentified.

The yttrium dihydroxy chloride preparation yielded two obviously different products in terms of appearance; however, both products, 9a and 9b of Table I, gave identical X-ray powder patterns without evidence either for the monoclinic form of $Y(OH)_2Cl$ or for $Y_3O(OH)_5Cl_2$. No attempts were made to prepare other rare earth members of the series isomorphous with either $La(OH)_2Cl$ or $Yb_3O(OH)_5Cl_2$.

In Table II are summarized our single-crystal lattice parameter data for the rare earth and yttrium hydroxy chlorides with the previously reported data for the hydroxy chlorides of yttrium. The first five entries of Table II contain the known monoclinic forms and they have either the $P2_1/m\text{-}C_{2h}^2$ or $P2_1\text{-}C_2^2$ space group with $Y(OH)_2Cl$ known[3] to have the former and $La(OH)_2Cl$ known to have the latter noncentrosymmetric space group. For the rare earth members the lattice parameters and volume have been fitted to curves of the form $y = E + FZ + GZ^2$, where Z is the atomic number of the metal. The coefficients E, F, and G are summarized in Table III and the deviations of the calculated cell edges from the measured values are indicated in Figure 1. For the orthorhombic form of $Y(OH)_2Cl$ our values of b apparently differ significantly from that of Klevtsova and coworkers. The origin of this difference is not known but may be due to the possible composition differences mentioned by the Russian workers,[2–4] *i.e.*, the substitution of OH^- for Cl^- in the structure.

Table III

Monoclinic Lattice Parameter *vs.* Atomic Number Least-Squares Fit

Parameter[a]	Coefficients E	F	G	Rms dev
a, Å	19.2235	−0.407829	0.00318454	0.0016
b, Å	9.0422	−0.136688	0.00084363	0.0006
c, Å	14.8152	−0.233256	0.00166672	0.0016
β, deg	18.212	3.51105	−0.032144	0.013
Vol, Å³	971.867	−24.9629	0.1880872	0.045

[a] Caution indicated in extrapolating a beyond $Z = 64$.

The stoichiometry of the compound labeled $Yb_3O(OH)_5Cl_2$ in Table II was presumed to be analogous, because of isomorphism, to that found chemically and confirmed crystallographically[4] for $Y_3O(OH)_5Cl_2$. These two compounds have the same systematic absences indicating either space group $Pnmm\text{-}D_{2h}^{13}$ or $Pnm2_1\text{-}C_{2v}^{7}$. The a direction is perpendicular to the hydrogen-bonded layers in the $Y_3O(OH)_5Cl_2$ compound and a is accordingly determined largely by the $OH \cdots Cl$ hydrogen bond. These values are essentially identical for the two compounds. The differences between the lengths of their b as well as between the lengths of their c axes are approximately what would be expected for the size difference between yttrium and ytterbium.

A typical thermal decomposition curve for the lighter rare earth dihydroxy chlorides of Table I consists of a single peak, 80–100° wide skewed toward higher temperatures, on a varying base line having an endothermic curvature. Gas evolution is associated with all thermal peaks observed, in a manner roughly proportional to the corresponding endothermic heat of decomposition, and correlates well with peak positions and with decomposition initiation temperatures. For well-formed dihydroxy chloride crystals these latter temperatures range from 350 to 390° with peaks at 434, 432, 433, and 460°

for the compounds of La, Nd, Sm, and Gd, respectively. Small and/or poorly formed crystals decompose at approximately 25° lower temperature. The heats of decomposition of the rare earth dihydroxy chlorides, associated primarily with the loss of water according to the typical reaction $La(OH)_2Cl = LaOCl + H_2O$, have been determined from area measurements. These are 28.9, 29.5, 31.6, and 28.1 cal/g for the dihydroxy chlorides of La, Nd, Sm, and Gd, respectively. Owing primarily to the width of the peak and strong endothermic curvature of the base line, the associated error for these heats of decomposition may be as large as 12%. The decomposition products of the above compounds are readily identified from X-ray powder photographs as the corresponding oxychlorides. This is supported by the agreement between the expected and observed ratio (weight before)/(weight after) for these compounds; a typical example is the observed ratio, 0.917, *vs.* the expected, 0.914, for $La(OH)_2Cl$. Laue photographs of the remains of single crystals of the above compounds (La–Gd) gave essentially good powder lines with some preferred orientation of the *c* axis of the oxychloride perpendicular to what was the cleavage planes of the dihydroxy chlorides. In the case of $Yb_3O(OH)_5Cl_2$ very slow decomposition of the needle mass starts at 278° (with no observable maximum below 500°) while large well-formed crystals (rectangular platelets) show no decomposition until the temperature is about 200° higher (gas effluent results). Powder patterns of the decomposed needle mass indicate only the presence of ytterbium oxide in a finely divided state (broad diffuse X-ray lines only). A visual examination of the well-formed crystals showed no apparent change upon being heated to 500° (at temperature; *ca.* 8 min) although some decomposition takes place at 550°. Thermal data for the yttrium analog, $Y_3O(OH)_5Cl_2$, obtained by Klevtsova, Kozeeva, and Klevtsov,[4] showed decomposition beginning at 465° with a shoulder and peak at 533 and 561°, respectively. These data not only suggest that well-formed crystals of $Yb_3O(OH)_5Cl_2$ are more stable than those of the yttrium compound, but also that these oxyhydroxy chlorides, by reason of their higher decomposition temperatures, peak shapes, and decomposition products, decompose by a different mechanism than the rare earth dihydroxy chlorides, possibly losing HCl and then H_2O as has been suggested.[4]

The X-ray powder diagrams of the two products (entry 9, Table I) in the preparation of $Y(OH)_2Cl$ appear to be identical but the thermograms of the two entries have pronounced differences. The cloudy hexagonal-like prisms give two separate smooth skew peaks (353 and 461°) as well as a small very shallow peak extending from about 220 to 290° with a broad maximum near 260°. Of the two high-temperature peaks the one at 461° is always more energetic, by a factor of 2–11. In contrast to the cloudy prisms, the clear, perfect crystals of nominally the same material give only a single peak at the higher temperature (478°). The powder patterns of the decomposition products of both crystal kinds of $Y(OH)_2Cl$ contain the YOCl lines as well as diffuse lines of Y_2O_3 with the clear crystals decomposing primarily to YOCl and the cloudy prisms decomposing primarily to Y_2O_3. Similarly Laue photographs of decomposed single crystals indicate that there is a preferred ordering of the [111] direction of Y_2O_3 and the [001] direction of YOCl perpendicular to the cleavage planes. Some of the cloudy prisms blacken upon heating to 550°. These variations in the $Y(OH)_2Cl$ preparation are presumably due to some contaminant, possibly the carbonates, as recently indicated by Caro[12] and/or the previously mentioned replacement of Cl^- by the hydroxyl group.

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(12) P. E. Caro and M. Lemaitro-Blaise, Proceedings of the Seventh Rare Earth Research Conference, Oct 25–30, 1968, Coronado, Calif., 1968, p 187.