very high electrical conductivity. An experimental and theoretical investigation of this is in progress.

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The Structure Refinement of La_2Te_3, a Th_3P_4 Type Structure[1]

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The thorium phosphide structure, Th_3P_4, occurs widely in the compounds of the lanthanides with tellurium, sulfur, phosphorus, bismuth, and others. The various cube edges are 8 to 10 Å., the space group is $I\bar{4}3d$, and there is only one variable parameter. This type of structure was first discussed by Meisel[2] and subsequently by Zachariasen[3] in relation to the compound Ce_2S_3. Kripyakevich[4] gave a detailed description of the structure in terms of the articulation of the polyhedra occurring in it. Carter[5] reviewed the Th_3P_4 structure from the standpoint of electrostatic energy and valence bond considerations and found that the x parameter of $^1/_{12}$, the idealized value for the single variable positional parameter, produces an unstable ionic structure in Ce_2S_3 and that a value of approximately 0.04 corresponds to a minimum in the electrostatic energy calculation. He concluded that a compound with a Th_3P_4 structure and an anion position of $^1/_{12}$ is essentially not ionic in nature, even though the bond distances obtained on the basis of this value are equal to the sum of the ionic radii.

The structure can be visualized as being made up of two kinds of anion tetrahedra surrounding a single cation. Both tetrahedra have a $\bar{4}$ axis of symmetry; one tetrahedron being large and elongated and the other being rather flat. With an anion parameter of $^1/_{12}$, the Th–P distances are all equal, but as the value drops below $^1/_{12}$, the large tetrahedron becomes longer and the flat tetrahedron smaller and less flat. The importance of this structure in the rare earth compounds prompted us to undertake a single crystal investigation to determine the exact value of the positional parameter of the 16-fold position of the ion in space group $I\bar{4}3d$; all other positions are fixed by symmetry.

Experimental Section

Samples for this determination were obtained from specimens which had been previously prepared during the investigation of the lanthanum–tellurium phase diagram.[6] Several crystals of irregular shape were selected from reacted batches of desired analyzed composition. The crystal used for data collection had dimensions of 0.11 mm. and 0.037 mm. at its widest and narrowest limits. The lattice constant for La_2Te_3 had previously been determined from powder diffraction data as 9.619 Å., and the value obtained from a Weissenberg film was in agreement with it. Flahaut[7] reports a value of 9.627 Å. for this composition. The crystal was mounted on a single crystal orienter and the diffraction data were collected using Zr-filtered Mo radiation with a scintillation counter and pulse height discrimination. The linear absorption coefficient of La_2Te_3 for Mo Kα is 262 cm.$^{-1}$ and $\mu R = 1.8$ when an average radius of 0.07 mm. is used for this crystal; no absorption corrections were made on the measured intensities.

There are $5^1/_3$ formula weights of La_2Te_3 in the unit cell and $10^2/_3$ sites of the equipoints 12(a) of $I\bar{4}3d$ are occupied by La, while Te is in 16(c), xxx; the single, variable, positional parameter and two isotropic temperature factors were determined using a full-matrix least-squares procedure with unit weights assigned to the structure factors. A test with two anisotropic temperature factors for La indicated essentially spherical symmetry. Approximately 100 general *hkl* reflections were collected because they overdetermine the problem sufficiently. The atomic scattering factors for lanthanum and tellurium were corrected for dispersion. The final discrepancy coefficient is 0.040 for the observed reflections listed in Table I, and Table II lists the parameters of the structure. The discrepancy factor, R, was

Table I

Observed and Calculated Structure Factors for La_2Te_3

h	k	ℓ	F_{obs}	$\lvert F_{cal}\rvert$	h	k	ℓ	F_{obs}	$\lvert F_{cal}\rvert$	h	k	ℓ	F_{obs}	$\lvert F_{cal}\rvert$
4	0	0	75	75	3	2	1	765	799	5	5	2	585	576
12	0	0	562	536	5	2	1	159	161	7	5	2	493	463
16	0	0	275	302	7	2	1	480	507	11	5	2	227	214
3	1	0	1052	1123	9	2	1	611	646	8	6	2	167	172
5	1	0	159	148	11	2	1	171	195	7	7	2	372	358
7	1	0	281	266	4	3	1	530	560	11	7	2	272	273
9	1	0	215	214	6	3	1	367	379	6	3	3	587	468
13	1	0	303	283	8	3	1	224	218	10	3	3	196	203
2	2	0	151	145	12	3	1	380	376	5	4	3	261	266
4	2	0	590	588	5	4	1	643	651	7	4	3	487	514
10	2	0	159	156	7	4	1	241	237	9	4	3	325	326
12	2	0	243	233	9	4	1	182	194	6	5	3	292	294
5	3	0	317	303	11	4	1	276	271	8	5	3	172	194
7	3	0	125	118	6	5	1	253	275	10	5	3	388	390
11	3	0	168	162	8	5	1	546	542	7	6	3	405	422
13	3	0	225	208	10	5	1	247	223	9	6	3	190	182
4	4	0	165	161	7	6	1	212	189	8	7	3	443	449
6	4	0	440	436	11	6	1	292	297	10	7	3	334	353
8	4	0	365	362	8	7	1	181	177	9	8	3	296	293
10	4	0	296	281	10	7	1	193	166	4	4	4	942	1069
12	4	0	220	226	9	8	1	153	149	8	4	4	404	414
7	5	0	490	494	11	8	1	249	249	12	4	4	381	361
9	5	0	485	516	4	2	2	722	733	7	5	4	245	263
11	5	0	241	243	8	2	2	521	507	9	5	4	281	286
6	6	0	512	520	12	2	2	323	320	8	6	4	285	281
12	6	0	218	196	3	3	2	535	529	6	5	5	567	585
9	7	0	263	264	5	3	2	597	594	7	6	5	227	248
11	7	0	379	364	7	3	2	304	284	8	6	6	495	524
8	8	0	777	768	11	3	2	250	232	9	7	6	370	367
2	1	1	192	197	13	3	2	276	272	9	9	6	316	316
6	1	1	833	824	6	4	2	447	419					
10	1	1	487	472	10	4	2	506	475					

Table II

Positional and Temperature Parameters of La_2Te_3

Atom	x	$\sigma(x)$	B, Å.^{2}	$\sigma(B)$
La	. . .		1.20	0.08
Te	0.0748	0.0002	0.96	0.08

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[1] Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, United States Air Force, under AFOSR Grant No. 62-237.

[2] K. Meisel, *Z. anorg. allgem. Chem.*, **240**, 300 (1939).

[3] W. H. Zachariasen, *Acta Cryst.*, **2**, 57 (1949).

[4] P. I. Kripyakevich, *Sov. Phys. Cryst.*, **7**, 556 (1963).

[5] F. L. Carter, Proceedings, Fourth Rare Earth Conference, Phoenix, Ariz., 1964; to be published.

[6] T. H. Ramsey, H. Steinfink, and H. J. Weiss, *Inorg. Chem.*, **4**, 1154 (1965).

[7] J. Flahaut, M. Guittard, M. Patrie, M. P. Pardo, S. M. Golobi, and L. Domange, *Acta Cryst.*, **19**, 14 (1965).

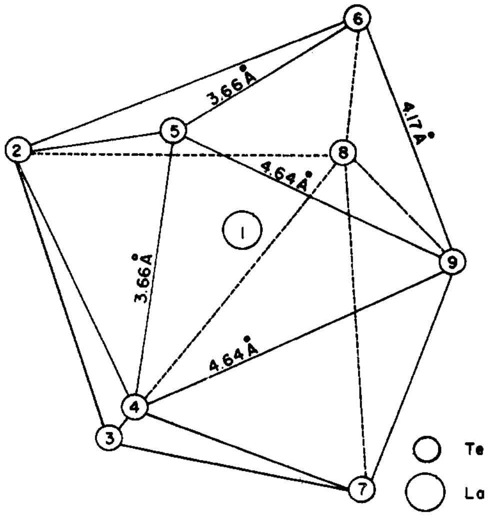

Figure 1.—Eightfold coordination of La in La_2Te_3. The coordination polyhedron can be considered as composed of two tetrahedra, one elongated and one flattened, or as an irregular octaverticon.

also calculated as a function of composition over the solid solution range La_3Te_4 to La_2Te_3, and the smallest value occurred for the composition La_2Te_3 for which the crystals had been originally selected.

Discussion of Structure

There are two different La–Te bond distances, 3.244 ± 0.0028 Å. and 3.418 ± 0.0028 Å., in the structure. The coordination polyhedron around La can be described in terms of two tellurium tetrahedra, an elongated one formed by atoms 6, 7, 3, 5 and a flat one formed by atoms 2, 8, 9, 4, Figure 1, or by the irregular octaverticon shown in Figure 1. Surrounding one La are eight other lanthanum atoms, all at a distance of 4.50 Å. from the central atom. The anion in this structure is coordinated to six lanthanum atoms which form a distorted octahedron.

Pauling's relation for bond length and bond number, $D_n = D_1 - 0.6 \log n$, was used to determine the relative strengths of the LaTe bonds. The term D_1 represents the sum of empirically derived metallic single bond radii and the values given by Pauling are 1.69 and 1.37 Å. for La and Te, respectively[8]; D_n is the observed bond length and n is the bond number. In Table III indicated electrostatic bond summations utilizing the derived parameter $x = 0.075$ are compared with those fixed by the idealized parameter of $^1/_{12}$. The sum of the bond numbers for each atom is very close to the formal valence when $x = 0.075$. It should be noted that these calculations do not take into account the missing lanthanum atoms in the deficient La_2Te_3 structure. One out of every nine La is absent and this produces a vacancy in the Te polyhedron. The polyhedra associated with the eight La closest neighbors to any given La polyhedron share with it one face from one or another of two nonequivalent sets of four triangular faces. Any instance of vacancy in two adjacent polyhedra would reduce electrostatic bond summations about some Te atoms to 1.25 (2, 4, 8, or 9 in Figure 1). When no two adjacent polyhedra are vacant, the minimum sum is 1.75. It seems probable that vacant sites are in fact ordered, at least locally. The over-all average Te bond number sum is 2. Occupancy of the polyhedra of the eight nearest La neighbors and the four next near La neighbors achieves this average in a smallest possible volume, *i.e.*, three-fourths of one unit cell.

TABLE III

RELATIVE BOND STRENGTHS OF La–Te BONDS IN La_2Te_3

Central atom	Coordinating atoms	D_n	n
		$x = 0.075$	
La	4 Te	3.24	0.5
	4 Te	3.42	0.25
			$\Sigma n = 3.0$
Te	3 La	3.24	0.5
	3 La	3.42	0.25
			$\Sigma n = 2.25$
		$x = 0.083$	
La	8 Te	3.33	0.354
			$\Sigma n = 2.83$
Te	6 La	3.33	0.354
			$\Sigma n = 2.12$

Holtzberg, Okaya, and Stemple[9] have reported a single crystal determination of the positional parameter in the compound Gd_2Se_3 of 0.0715 and in the compound La_3Se_4 (which contains no vacancies) of 0.075. These findings indicate that in rare earth compounds having a thorium phosphide structure considerable covalent bonding exists and the variable positional parameter deviates from the ideal value of 0.083 and is near 0.075.

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(8) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).

(9) F. Holtzberg, Y. Okaya, and N. Stemple, Abstracts, American Crystallographic Association Meeting, Gatlinburg, Tenn., 1965.

CONTRIBUTION FROM SHELL DEVELOPMENT COMPANY,
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Reaction Product from Rhodium Trichloride and Acrylonitrile

BY K. C. DEWHIRST

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The reduction of rhodium trichloride by ethanol in the presence of olefins[1-3] has frequently been employed for the preparation of π complexes of rhodium(I). We now wish to report that the use of acrylonitrile in this reaction gives rise to a stable σ complex of rhodium(III). Only a few organorhodium complexes of this general type are known[4,5] and have been prepared by different routes.

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(1) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(2) R. Cramer, *Inorg. Chem.*, **1**, 722 (1962).

(3) G. N. Schrauzer and K. C. Dewhirst, *J. Am. Chem. Soc.*, **86**, 3265 (1964).

(4) R. F. Heck, *ibid.*, **86**, 2796 (1964).

(5) J. Chatt and A. E. Underhill, *J. Chem. Soc.*, 2088 (1963).