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The Crystal Structures of Some of the Rare Earth Carbides

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A study of the rare earth-carbon systems has been made. The existence of the reported LaC_2 , CeC_2 , PrC_2 , NdC_2 and SmC_2 , and the Ce_2C_3 has been confirmed. The existence of the tetragonal CaC_2 type structure for the other rare earth dicarbides has been shown. The lattice constants of these compounds decrease in a regular fashion, except for the YbC_2 , whose lattice parameters lie between those of HoC_2 and ErC_2 . The body-centered cubic Pu_2C_3 type structure has been found to exist in all of the rare earths from La to Ho. The lattice constants decrease in a normal manner, except for Ce_2C_3 , whose lattice parameter is smaller than would be expected. A new rare earth carbide has been found, R_3C , which is similar to the face-centered cubic NaCl type structure, except that it is deficient in carbon. This compound appears to exist over a range of composition, *i.e.*, in the case of yttrium it was found to vary from $\text{YC}_{0.25}$ to $\text{YC}_{0.40}$. This compound has been found to exist in the rare earth-carbon systems of Sm to Lu, and the lattice parameters decrease in a regular manner. No X-ray evidence was found for the existence of this lower carbide in the La-, Ce-, Pr- and Nd-C systems.

Introduction

The crystal structures of several tetragonal rare earth dicarbides (LaC_2 , CeC_2 , PrC_2 , NdC_2 and SmC_2) and a hexagonal YC_2 have been known for several years.² Recently the existence of other rare earth carbon compounds, CeC ,³ Ce_2C_3 ³ and CeC_3 ,⁴ have been reported. CeC was reported to be face-centered cubic (NaCl type) with a lattice constant of 5.130 Å.; Ce_2C_3 was found to be body-centered cubic (plutonium sesquicarbide type⁵) with

$a_0 = 8.455$ Å., while no structural data have been reported for CeC_3 . In a study of the lanthanum-carbon system⁶ only two compounds were found, La_2C_3 and LaC_2 . The structural details of these two carbides were determined using X-ray and neutron diffraction techniques.⁷

Experimental

Materials.—The rare earth metals, 99.9% pure, were prepared by metallothermic reduction methods described by Spedding and Daane.⁸ In general, the metals were used in the form of filings or finely divided chips since it was easier to achieve homogeneous alloys by arc melting compressed cylinders of the metal filings and carbon powder. The carbon was prepared in the form of a powder by turning spectroscopic electrodes on a lathe.

(1) Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Based in part on a dissertation submitted by Karl Gschneidner, Jr., to the Graduate School, Iowa State College, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

(2) M. von Stackelberg, *Z. Elektrochem.*, **37**, 542 (1931).

(3) L. Brewer and O. Krikorian, *J. Electrochem. Soc.*, **103**, 38 (1956).

(4) J. C. Warf, paper presented at the ACS Northwest Regional Meeting, Seattle, Washington, 1956; Abstracted in *Chem. Eng. News*, **34**, 3446 (1956).

(5) W. H. Zachariasen, *Acta Cryst.*, **5**, 17 (1952).

(6) F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, "The Lanthanum-Carbon System," to be published.

(7) M. Atoji, *et al.*, *THIS JOURNAL*, **80**, 1804 (1958).

(8) F. H. Spedding and A. H. Daane, *J. Metals*, **6**, 504 (1954).

Preparation of Samples.—The samples were prepared by two techniques. The first method was employed for rare earth metals which have boiling points above 2000°. Approximately 200 mg. of the metal weighed out to an accuracy of ± 0.2 mg. carbon was weighed (accurate to ± 0.2 mg.) and added to the metal to give the desired composition. The metal and carbon were mixed and then compressed in a $\frac{3}{16}$ -inch diameter die under a pressure of 25–40 tons/in.². Because of the reactivity of Ce and La in air, the filings of these metals were prepared in a vacuum dry box and were removed only for weighing and compressing. The weighed compacts were arc-melted under an atmosphere of He or Ar. The second method, which consisted of heating weighed amounts of the metal and carbon in a Ta bomb at 1200–2000° for 2–24 hours, was used for preparing the Sm, Tm and Yb carbides.

The carbides are quite unstable in air and for this reason X-ray samples must be prepared in an inert atmosphere. The alloys were placed in a vacuum dry box and the system evacuated to a pressure of 20–30 μ Hg. A positive pressure of Ar or He was maintained on the dry box while working with the specimens. Any oxide coating first was removed from the alloy by scraping it clean with a razor blade. The carbide was crushed in a hardened tool steel mortar and then ground to approximately 350-mesh powder with an agate mortar and pestle. After the capillary tubes were filled, the system was opened and the tubes were sealed by fusion of the open end. In the short space of time that the tube is exposed to the atmosphere no reaction was detected between the sample and the atmospheric gases, because of the inert atmosphere in the capillary tube. While the capillary tubes were being filled, back reflection samples of the alloy were prepared by spreading a thin layer of the alloy over the adhesive side of cellophane tape. A second piece of this tape was fastened back-to-back to the first, thus sealing the alloy between the two pieces of tape. No appreciable oxidation of the sealed specimens was detected after 10 hr. exposure to air. Samples with low carbon contents (those with less carbon than that equivalent to the theoretical composition RC, *i.e.*, 8% C for La to 6.5% C for Lu and 11% for Y) were prepared in the manner described above, except that the samples were filed instead of crushed. X-Ray patterns of these filed samples were taken without annealing, but if the back reflection lines were diffuse the samples were then annealed at 400 \pm 25° for 20–100 hr. before a second pattern was taken from which the precise lattice constants were obtained.

Chemical Analysis.—Analyses of these alloys for their carbon content were carried out by igniting the weighed alloy to the corresponding oxide. From the weight of the oxide the amount of the metal in the alloy is calculated directly; the carbon concentration was obtained by difference to an accuracy of $\pm 0.05\%$. The details of this procedure are described in another paper.⁹

X-Ray Methods.—A 114.59 mm. Debye-Scherrer camera was used for the structure determinations and in some cases it also was used for determining lattice parameters. A symmetrical focusing back reflection camera, 120 mm. in diameter, was used to obtain diffraction patterns for a more accurate lattice constant. A constant flow of helium through the camera served to reduce air scattering of X-rays and to reduce the rate of corrosion of the samples. All of the carbides were examined with both cameras, but in many cases the patterns obtained using the Debye-Scherrer camera were much sharper and these were used to determine the lattice parameters. Copper K α radiation was used for all samples. In the case of La, Ce and Pr a 0.5-mil sheet of aluminum foil was placed between the sample and film to reduce the background due to X-ray fluorescence.

The X-ray intensity I was calculated according to the formula $I \approx jLF^2T$ where j is the multiplicity; L is the combined Lorentz and polarization factor; F is the structure factor; and T is the temperature factor determined according to the method of Bradley and Lu.⁹

The lattice parameters for the cubic materials were determined by either the Bradley and Jay¹⁰ or the Nelson and Riley¹¹ extrapolation method. The probable error for the

lattice constants of cubic materials was determined using the equations

$$\delta a_0 = \frac{(\delta S)Sa_0}{(8R)^2} \text{ for the back reflection camera}$$

and

$$\delta a_0 = \frac{(\delta S)Sa_0}{(4R)^2} \text{ for the Debye-Scherrer camera}$$

where S is the distance between the last pair of lines on the diffraction pattern; a_0 is the extrapolated lattice constant; R is the camera radius and δS is the error in measuring a given line. Of these terms only αS is unknown; it was found that a value of ± 0.2 mm. for δS will give a probable error within which 9 of 10 observations would fall. The lattice parameters for the tetragonal compounds were calculated by Cohen's least-squares method,¹² while the probable error was calculated according to the method of Jette and Foote.¹³

Results and Discussion

This investigation confirmed the existence of Ce₂C₃ and the dicarbides of La, Ce, Pr, Nd and Sm. The existence of the tetragonal structure for the other rare earth dicarbides (except for Pm and Eu) and also YC₂ has been shown. The body-centered cubic sesquicarbide has been found in the rare earth-carbon systems from La to Ho (except for Pm and Eu). Also a new rare earth carbide has been prepared, the tri-rare earth carbide, R₃C. This compound exists in the rare earth-carbon systems from Sm to Lu (except for Eu) and in the Y-C system.

The Tri-rare Earth Carbide.—This carbide was first observed while investigating some low Y-C alloys. Microscopic examination indicated that the composition of this lower carbide varied from YC_{0.25} (Y₄C) to YC_{0.40} (Y₅C₂); this carbide will be referred to as the "tritytrium carbide," Y₃C, since this composition lies approximately midway between the two limits. No attempt was made to establish the range of solid solubility of the tri-rare earth carbides, but the authors believe that these compounds have approximately the same limits of solubility as the tritytrium carbide. Indexing of the Y₃C X-ray pattern showed only face-centered cubic lines. A density measurement of an alloy of the composition YC_{0.40} indicates that there are 4Y and 1.6C atoms per unit cell. Since intensity measurements were taken from the X-ray patterns of this sample, all calculations were based on this Y:C ratio. Intensity data were obtained by visual comparison of the diffracted lines on four Debye-Scherrer diagrams of different timed exposures. There are two possible sets of positions that can be occupied by the C atoms: they can randomly occupy: (1) 1.6 of the 4-octahedral holes, NaCl-type, space group Fm3m (O_h⁵) or (2) 1.6 of the 8-tetrahedral holes, sphalerite (ZnS) type, space group F43m (T_d²). There is the possibility of an ordered structure but since no extra lines were observed, this possibility was discarded. The intensity ratios of various reflections, shown in Table I, reveal that the C atoms occupy the octahedral holes.

Interstitial compounds which have non-metallic atoms occupying only some of the octahedral or tetrahedral holes are not uncommon. The nitrides of W, Mo, Mn and Fe, the hydrides of Zr, Ti and Pd

(9) A. J. Bradley and S. S. Lu, *Z. Krist.*, **96**, 20 (1937).

(10) A. J. Bradley and A. H. Jay, *Proc. Phys. Soc. (London)*, **44**, 563 (1932).

(11) J. B. Nelson and D. P. Riley, *ibid.*, **57**, 160 (1945).

(12) M. U. Cohen, *Rev. Sci. Instr.*, **6**, 68 (1935).

(13) E. R. Jette and F. Foote, *J. Chem. Phys.*, **3**, 605 (1935).

TABLE I
INTENSITY RATIOS OF VARIOUS REFLECTIONS FOR THE TWO
POSSIBLE SPACE GROUPS OF Y_2C_3

Ratio	Obsd.	Calcd.	
		Octahedral holes Fm3m	Tetrahedral holes F43m
$\frac{I_{111}}{I_{220}}$	1.50	1.58	2.32
$\frac{I_{220}}{I_{311}}$	1.05	1.12	1.01
$\frac{I_{311}}{I_{420}}$	0.65	0.98	1.22
$\frac{I_{422}}{I_{511,333}}$	1.00	1.02	0.95

and the carbides of Ta, Nb, Mo and W have been known for some time to have these deficient type structures. The tritrium carbide and the tri-rare earth carbides are of the Fe_3N type structure; the *Strukturbericht* notation is L_1' .

The lattice parameters of the carbon-rich side of the tri-rare earth carbides (Table II) were calculated from diffraction patterns of alloys containing slightly more carbon than the stoichiometry R_3C_2 . These diffraction patterns contained a few extra lines which could be indexed as those corresponding to the strongest lines of the respective sesquicarbide. A comparison of the radii derived from the metal-to-metal distances in the R_3C compounds with the metallic radii (Table II) shows that the metal-to-metal distances are expanded on an average of 1.3% by the addition of carbon to the metal to form the lower carbide. A notable exception is Yb which undergoes a contraction of 9.02%. It should be interesting to see how this increase will affect the various physical properties, i.e., magnetic properties, resistivity, Hall coefficient, etc. The Gd_3C is ferromagnetic at room temperature, while Tb_3C appears to be antiferromagnetic at liquid nitrogen temperature. Further studies of the magnetic properties of these compounds are being carried out at this Laboratory.

TABLE II

THE LATTICE CONSTANTS, METALLIC RADII AND METAL-TO-CARBON DISTANCES OF THE TRI-RARE EARTH CARBIDES AND A COMPARISON OF THE RADII AS CALCULATED FROM THE R_3C COMPOUNDS AND THE RARE EARTH METALS

Rare earth	a_0 (Å.)	$r_{R_3C}^a$ (Å.)	r_M^b (Å.)	% Change	D_{M-C} (Å.)
Sm	5.172 ± 0.010	1.829	1.802	1.50	2.586
Gd	5.126 ± .005	1.812	1.802	0.55	2.563
Tb	5.107 ± .002	1.806	1.782	1.35	2.554
Dy	5.079 ± .005	1.796	1.773	1.30	2.540
Ho	5.061 ± .002	1.789	1.766	1.30	2.530
Er	5.034 ± .001	1.780	1.757	1.31	2.517
Tm	5.016 ± .004	1.773	1.746	1.55	2.508
Yb	4.993 ± .001	1.765	1.940	-9.02	2.496
Lu	4.965 ± .001	1.755	1.734	1.21	2.482
Y	5.102 ± .002	1.804	1.801	0.17	2.551
Y(Y-rich side)	5.127 ± .001				

^a Metallic radii calculated from the R_3C lattice constants.

^b Metallic radii calculated from the lattice constants of the metals.¹⁴

(14) F. H. Spedding, A. H. Daane and K. W. Herrmann, *Acta Cryst.*, **9**, 559 (1956).

The reason for the existence of this tri-rare earth carbide in some of the rare earth-carbon systems, but not in others, is not completely clear. It has been shown that for atoms to occupy the octahedral holes, the ratio of the radii of the small atoms to the large atoms must lie between 0.414 and 0.732.¹⁵ The carbon radius may be obtained by subtracting the metallic radii (calculated from the lattice constants of the pure metals)¹⁴ from the corresponding metal-to-carbon distance; the calculated carbon radius obtained from these nine carbides, excluding Yb, varied from 0.784 to 0.748, with a mean value of 0.763 Å. Using the mean value to compute the carbon to rare earth radius ratios, the following values were obtained: 0.406, 0.418, 0.417, 0.419, 0.423, 0.424 and 0.440 for La, Ce, Pr, Nd, Sm, Y and Lu, respectively. Only the radius ratio for La is less than the critical value (0.414), but the values for Ce, Pr and Nd are just slightly greater (within 1.2%), while the radius ratios for the other rare earths (Sm to Lu) and yttrium are more favorable. It is possible that the size effect does determine whether or not this compound will be formed. Also, the fact that the first four rare earths^{14,16} are hexagonal closest-packed with a double *c*-axis while the other hexagonal rare earth metals¹⁴ have a normal *c*-axis may be significant.

The Rare Earth Sesquicarbides.—The structural details of the La_2C_3 compound, including the carbon positions, have been determined by X-ray and neutron diffraction techniques described in a paper from this Laboratory.⁷ The rare earth sesquicarbides from La to Ho (Pm and Eu were not examined) have the body-centered cubic Pu_2C_3 type structure (the *Strukturbericht* notation is $D5_a$). The lattice parameters and X-ray densities are given in Table III. The lattice constant for Ce_2C_3 agrees well with the value reported by Brewer and Krikorian.³ One notes that the lattice parameter of the cerium compound lies between the values for the Nd and Sm compounds. This may indicate that Ce is partially or wholly tetravalent in this compound. It appears that the other rare earths and yttrium form a sesquicarbide whose structure has not been determined, but which probably has less than either hexagonal or tetragonal symmetry. The sesquicarbides of Ho, Er, Tm and Lu appear to be isostructural with the Y_2C_3 compound. X-Ray patterns of Ho_2C_3 have been taken showing either the Pu_2C_3 or Y_2C_3 type structure, indicating that Ho_2C_3 is dimorphic. Ytterbium also forms an intermediate carbide, perhaps of the Yb_2C_3 composition, but it does not appear to be isostructural with either the Pu_2C_3 or the Y_2C_3 type compounds.

The Rare Earth Dicarbides.—von Stackelberg² showed that several of these rare earth dicarbides were isostructural with CaC_2 . Recently, Atoji and co-workers from this Laboratory, using X-ray and neutron diffraction techniques, verified this structure for LaC_2 ; they also located the carbon atoms and determined the bond distances with

(15) A. F. Wells, "Structural Inorganic Chemistry," 2nd Ed., Oxford, 1950, p. 66.

(16) Cerium begins to form a hexagonal closest-packed structure with a double *c*-axis at $15 \pm 5^\circ$: C. J. McHargue, H. L. Yakel, Jr., and L. K. Jetter, *Acta Cryst.*, **10**, 832 (1957).

TABLE III
LATTICE CONSTANTS AND X-RAY DENSITIES FOR SOME
RARE EARTH SESQUICARBIDES

Rare earth	Lattice constant, a_0		X-ray density ^a (g./cm. ³)
	M-rich side (Å.)	C-rich side (Å.)	
La ^b	8.8034 ± 0.0004	8.8185 ± 0.0004	6.079
Ce ^c	8.4476 ± 0.0004		6.969
Pr	8.5731 ± 0.0005	8.6072 ± 0.0006	6.621
Nd	8.5207 ± .0011	8.5478 ± .0006	6.902
Sm	8.3989 ± .0012	8.4257 ± .0012	7.477
Gd	8.3221 ± .0005	8.3407 ± .0006	8.024
Tb	8.2434 ± .0005	8.2617 ± .0007	8.335
Dy	8.198 ± .002		
Ho		8.176 ± .003	8.892

^a Computed from the lattice constant of the carbon-rich side and assuming the stoichiometry to be R_2C_3 . ^b Density at the theoretical composition of La_2C_3 is 6.081 g./cm.³ ^c Ce exhibits no solid solubility.

precision.⁷ All of the rare earth dicarbides examined in this study and also YC_2 have been shown to have the body-centered tetragonal CaC_2 type structure, the *Strukturbericht* notation is C 11a. The lattice parameters, c/a ratios and X-ray densities for these compounds are listed in Table IV. The values obtained in this study of the di-

TABLE IV
THE LATTICE CONSTANTS, c/a RATIOS AND X-RAY DENSITIES OF THE RARE EARTH DICARBIDES

Rare earth	Lattice constants		c/a ratio	X-Ray density (g./cm. ³)
	a_0 (Å.)	c_0 (Å.)		
La	3.934 ± 0.002 (3.92) ^a	6.572 ± 0.001 (6.56) ^a	1.671	5.319 (5.35) ^a
Ce	3.878 ± .001 (3.88) ^a	6.488 ± .002 (6.49) ^a	1.673	5.586 (5.56) ^a
Pr	3.855 ± .002 (3.85) ^a	6.434 ± .004 (6.42) ^a	1.669	5.728 (5.73) ^a
Nd	3.823 ± .001 (3.82) ^a	6.405 ± .003 (6.37) ^a	1.675	5.970 (6.00) ^a
Sm	3.770 ± .001 (3.76) ^a	6.331 ± .003 (6.29) ^a	1.679	6.434 (6.50) ^a
Gd	3.718 ± .001	6.275 ± .003	1.688	6.939
Tb	3.690 ± .002	6.217 ± .005	1.685	7.176
Dy	3.669 ± .001	6.176 ± .003	1.683	7.450
Ho	3.643 ± .001	6.139 ± .002	1.685	7.701
Er	3.620 ± .001	6.094 ± .003	1.683	7.954
Tm	3.600 ± .002	6.047 ± .007	1.680	8.175
Yb	3.637 ± .004	6.109 ± .010	1.680	8.097
Lu	3.563 ± .001	5.964 ± .006	1.674	8.728
Y	3.664 ± .001 (3.80) ^{a,b}	6.169 ± .004 (6.57) ^{a,b}	1.684	4.528 (4.58) ^{a,b}

^a Data of von Stackelberg.² Converted to the body-centered tetragonal lattice to conform with space group given in the "International Tables for X-Ray Crystallography," Vol. I ($a_{\text{tet}} = 0.7071a_{\text{fcc}}$). Also converted from kX. units to ångström units. ^b von Stackelberg stated that YC_2 was probably hexagonal.²

carbides of La, Ce, Pr, Nd and Sm agree well with those reported by von Stackelberg²; however, the YC_2 was found to be tetragonal and not hexagonal as suggested by von Stackelberg. The lattice parameters of YC_2 lie between those of DyC_2 and HoC_2 . YbC_2 appears to have abnormal lattice parameters, which lie between the values of HoC_2 and ErC_2 . This might indicate that Yb is partially or wholly divalent in this compound. It is of interest to point out that while annealing some YbC_2 in a high vacuum, this material decomposed at $800 \pm 100^\circ$ to gaseous ytterbium and carbon; this fact has been applied as a means of preparing

and separating Yb from a mixture of rare earth oxides.¹⁷ Some preliminary hydrolytic studies of YbC_2 also seem to indicate the valence is less than +3 for Yb in this compound; the results are discussed later in this paper.

X-Ray Study of Some La-, Ce-, Pr- and Nd-C Alloys.—A thorough study was undertaken to confirm the existence of the reported RC and RC_3 compounds^{3,4} and to examine the R_3C region for the first four rare earths. The La-C equilibrium diagram is discussed in detail in another paper,⁶ where it is shown by equilibrium and quenching studies that only two compounds, La_2C_3 and LaC_2 , exist and that there is no detectable solid solubility of carbon in lanthanum except at high temperatures (maximum solubility was about 0.4% carbon in lanthanum at 875°). The results of an X-ray study of several Ce-, Pr- and Nd-C alloys (Table V) show that the tri-rare earth carbide does not exist in these three systems under the described conditions. These results indicate that the CeC reported by Brewer and Krikorian³ was probably a solid solution of carbon in cerium. Their lattice constant, $a_0 = 5.130$ Å., is identical with the value found for the Ce metal saturated with carbon (Table V). Also, this study does not

TABLE V
X-RAY STUDY OF SOME Ce-, Pr- AND Nd-C ALLOYS^a

Composition of alloy, %	Phase present
Cerium	
100	fcc Ce, $a_0 = 5.1612^b$
0.5	fcc Ce, $a_0 = 5.140$
1.1	fcc Ce, $a_0 = 5.133$
2.78	(Theor. composition of Ce_3C)
2.8	fcc Ce, $a_0 = 5.130$; bcc Ce_2C_3 , $a_0 = 8.448$
7.89	(Theor. composition of CeC)
7.9	fcc Ce, $a_0 = 5.130$; bcc Ce_2O_3 , $a_0 = 8.449$
11.39	(Theor. composition of Ce_2C_3)
12.0	bcc Ce_2C_3 , $a_0 = 8.4476$; bct CeC_2 (only a few weak lines)
14.63	(Theor. composition of CeC_2)
14.6	bct CeC_2 , $a_0 = 3.878$, $c_0 = 6.488$
19.0	bct CeC_2 , $a_0 = 3.878$, $c_0 = 6.488$; free C (determined by chemical and microscopic analyses)
20.45	(Theor. composition of CeC_3)
Praseodymium	
100	hex Pr, $a_0 = 3.6725$, $c_0 = 11.835^b$
2.76	(Theor. composition of Pr_3C)
4.0	hex Pr^c ; bcc Pr_2C_3
7.85	(Theor. composition of PrC)
7.9	hex Pr^c ; bcc Pr_2C_3
Neodymium	
100	hex Nd, $a_0 = 3.6579$, $c_0 = 11.799^b$
2.0	hex Nd ^c ; bcc Nd_2C_3 (only a few weak lines)
2.70	(Theor. composition Nd_3C)
2.8	hex Nd ^c ; bcc Nd_2C_3
7.68	(Theor. composition NdC)
7.7	hex Nd (few weak lines); bcc Nd_2C_3

^a All alloys were examined in the quenched form (as arc-melted) as well as in the annealed condition. ^b Lattice constants were taken from reference 14. ^c Lattice constants same as for the pure metal.

confirm the existence of the silvery CeC reported by Warf.⁴ Several high carbon Ce-C and La-C alloys were examined in an attempt to confirm the existence of CeC₃ reported by Warf.⁴ Microscopic examination and chemical and X-ray analyses show that alloys near the tricarbidic composition (either quenched or slow cooled from the molten state) contain only free carbon and the rare earth dicarbide. It is possible that the presence of hydrogen in Warf's method of preparation may be the cause of this difference.

Hydrolytic Studies.—Investigation of gases liberated when various carbides react with water or dilute acids is in progress in this Laboratory. Examination of the R₃C indicates that the carbon atoms are approximately 3.5 Å. apart if carbon atoms occupy adjacent octahedral holes and, therefore, one would expect these compounds to form methane and hydrogen gas on hydrolysis. Mass spectrometric analysis of the gases liberated upon hydrolysis shows that only methane and hydrogen are formed, indicating that the R₃C compounds are methanides. Both the R₂C₃ and RC₂ compounds may be classified as acetylides, although they do not yield pure C₂H₂. The La₂C₃ yields approximately 50% C₂H₂, compared to 70% for LaC₂, and the amount of hydrogen liberated by the former is 2.5 times that of LaC₂. It is also significant that some C₃H_x (x = 4, 6 and 8) hydrocarbons are formed only from La₂C₃. The relative amounts of hydrogen liberated can be explained if one assumes that C₂⁻ anions are formed and the

extra La valence electrons contribute to the conduction band. For the sesquicarbide the number of conducting electrons per La atom is 1.5 and 1.0 for the dicarbide. Since the number of valence electrons per atom in the conduction band is related directly to the amount of hydrogen liberated, one would expect a higher yield of hydrogen for La₂C₃, and this is what is observed. The relative amount of C₂H₂ liberated can be explained by the number of C₂⁻ groups per La atom. There is 1.0 group per La for LaC₂ and 0.75 for La₂C₃ and, therefore, the dicarbide would be expected to liberate more C₂H₂, which it does. Hydrolytic studies of YbC₂ show a slight increase in the amount of C₂H₂ and the absence of H₂ compared to LaC₂. The results of these hydrolytic studies and the fact that the lattice parameters of YbC₂ are abnormally small would indicate that YbC₂ is probably more closely related to the alkaline earth metal dicarbides than to the rare earth dicarbides. Similarities between the alkaline earth metals and ytterbium, and some of their compounds have been noted in other studies.

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