Six measurements were made of the heat of solution of sodium fluoride, 1,300, 1,320, 1,350, 1,370, 1,280 and 1,280. Two measurements were made of reaction 15 (−3.5 and −5.1 cal./mole) to confirm that the heat is approximately zero, as previously reported.[9]

Heat-capacity data from the sources noted earlier[1,10–12] were used to correct ΔH_{16} to 298.15°K. Combination with heat of formation data[13] for NaCl(c), $HF.5{\cdot}716H_2O$(sol) and $HCl{\cdot}12{\cdot}731H_2O$(sol) led to a value of −136.3 ± 0.2 kcal./mole for the heat of formation of sodium fluoride from the elements at 298.15°K.

$$Na(c) + 1/2F_2(g) = NaF(c) \qquad (17)$$

This differs by 0.3 kcal./mole from the value chosen by Rossini and co-workers,[13] based upon older work.

Discussion

The heat of formation of aluminum fluoride (derived from the work of Gross and co-workers[14]) and the present data suffice for obtaining the heat of formation of cryolite from its constituent fluorides. (The author had hoped to check the value for aluminum fluoride; but this proved impossible with available apparatus, as no suitable solvent could be found.)

Combination of reactions 8 and 10 with the heats of formation of aluminum fluoride and sodium fluoride leads to reactions 18 and 19, the formation

$$2.96NaF(c) + AlF_3(c) = Na_{2.96}AlF_{5.96}(c), \quad \Delta H_{298.15} = -20.1 \text{ kcal./mole} \qquad (18)$$

$$3NaF(c) + AlF_3(c) = Na_3AlF_6(c), \quad \Delta H_{298.15} = -20.3 \text{ kcal./mole} \qquad (19)$$

of $Na_{2.96}AlF_{5.96}$(c) and of stoichiometric cryolite from the constituent fluorides. Application of King's[1] entropy data and O'Brien and Kelley's[2] high temperature heat content data to reaction 19 shows that the free energy of combination of the fluorides varies from −21.6 kcal./mole at 298° to −29.1 kcal./mole at 1400°K.

Berkeley 4, California

[Contribution No. 544 from the Institute for Atomic Research and Department of Chemistry, Iowa State College. Work was Performed in the Ames Laboratory of the U. S. Atomic Energy Commission]

The Structures of Lanthanum Dicarbide and Sesquicarbide by X-Ray and Neutron Diffraction

By Masao Atoji, Karl Gschneidner, Jr., A. H. Daane, R. E. Rundle and F. H. Spedding

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Lanthanum dicarbide, with a structure of the calcium carbide type is body-centered tetragonal, $a = 3.934 \pm 0.002$ Å., $c = 6.572 \pm 0.003$ Å. The C–C distance of the C_2 group is 1.28 ± 0.02 Å., intermediate between double and triple bond C–C distances. Lanthanum sesquicarbide is body-centered cubic with the plutonium sesquicarbide ($D5_c$-type) structure, and a lattice constant between 8.803 and 8.819 Å. It also contains C_2 groups but with a C–C distance (1.32 ± 0.03 Å.) about that of a double bond. A possible relation between electron density and C–C distance is noted. Carbon positions in both structures were determined by neutron powder data, and were refined by a statistical method based on the least squares method.

Introduction

X-Ray powder data have shown that LaC_2 is isostructural with calcium carbide. The body-centered tetragonal cell contains two formula units; the already reported space group is D_{4h}^{17}–I 4/mmm.[1] There are a number of metal carbides with this structure, but in none has the C–C distance been determined accurately due to the relatively small X-ray scattering power of carbon. This distance is interesting due to its relationship to the acetylene ion, $C_2^{=}$.

The cubic sesquicarbides are related in that they also contain C_2 groups or ions. U_2C_3,[2] Pu_2C_3[3] and Ce_2C_3[4] have been reported previously. La_2C_3 was discovered in an examination of the La–C system.[5] The body-centered cell contains eight formula units, and the reported space group is T_d^6–$I\bar{4}3d$. There is only one metal parameter, and this has been well established for Pu_2C_3. From X-ray data the one carbon parameter can only be guessed, and the reported value for Pu_2C_3 leads to a C–C distance of 1.5 Å., which turns out to be considerably too long for lanthanum sesquicarbide. For reasons pointed out below, more data on several of these compounds would be of interest.

Preparation of Diffraction Samples.—The carbides used in this investigation were prepared from 99+% lanthanum and high purity graphite by arc melting under a helium atmosphere. Preparation, analyses and methods of handling are described fully elsewhere.[5]

X-Ray and neutron samples were obtained by crushing the carbide preparations in a hardened tool-steel mortar within a carefully flushed dry-box under a positive pressure of dry argon or helium. X-Ray capillary tubes were filled inside the dry-box, but were removed and sealed in air. This caused no contamination of the samples because of the inert atmosphere in the capillaries. Neutron diffraction samples were placed in special vanadium tubes and capped in the dry-box. Back-reflection camera samples were prepared in the dry-box by spreading the carbide on cellophane tape and sealing it with a second strip of tape. No appreciable oxidation of such samples was detected after 10 hours in air.

Lanthanum Dicarbide

Unit Cell and Density.—Accurate lattice constants for lanthanum dicarbide were obtained using a precision, self-focusing back-reflection

(1) M. von Stackelberg, *Z. physik. Chem.*, **B9**, 437 (1930).

(2) M. W. Mallett, A. V. Gerds and D. A. Vaughan, *J. Electrochem. Soc.*, **98**, 505 (1951).

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

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

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

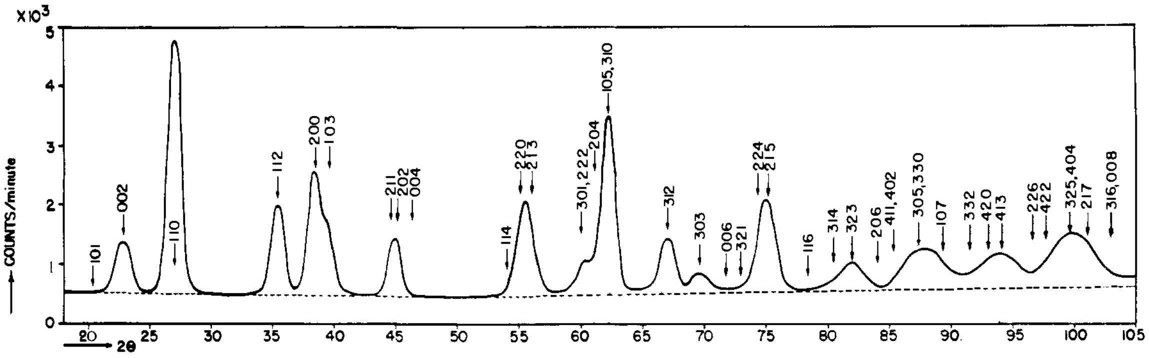

Fig. 1.—Neutron scattering curve for LaC_2.

powder camera and Cu $K\alpha$ radiation. A foil (1.0 mil of nickel or 0.5 mil of aluminum) was placed over the film to reduce the background due to fluorescence of lanthanum, and a constant flow of helium through the camera was used to reduce corrosion of the sample and air scattering of X-rays.

The lattice parameters were refined by application of the method of least squares, yielding $a = 3.934 \pm 0.002$, $c = 6.572 \pm 0.003$ Å. These results are more precise but in good agreement with those previously reported.[1] The X-ray density is 5.318 compared to a pycnometric density of 5.297 g./cm.[3].

Lattice constants of the other available rare earth dicarbides have been determined, and these data have been reported separately.[6]

Structure Determination.—Neutron powder diffraction data (Fig. 1), were obtained using the neutron diffraction spectrometer of the Argonne National Laboratory. The diffraction maxima were successfully indexed on the basis of the X-ray unit cell using a neutron wave length of 1.277 Å. with a maximum error of 0.005 Å. The integrated intensities were obtained by integration over the diffraction peaks using a polar-planimeter. The Lorenz factors were applied and the observed jF^2 values, where j is the multiplicity factor and F is the structure factor, were thus obtained.[7]

The scattering lengths used for the calculated structure factor are 0.83×10^{-12} cm. and 0.66×10^{-12} cm. for La[8] and C,[9] respectively.

The atomic coördinates are: (000, $^1/_2{}^1/_2{}^1/_2$) for La and (000, $^1/_2{}^1/_2{}^1/_2$) ± (00z) for C. The structure factors F were calculated for several z-parameters corresponding to a wide range of C–C distances. The discrepancy factors R_1 and R_2 are plotted as a function of the C–C distance in Fig. 2, where

$$R_1 = \frac{\sum\limits_u \left(\sum\limits_g jF^2{}_{\text{obs}} - \sum\limits_g jF^2{}_{\text{calcd}} \right)}{\sum\limits_u \sum\limits_g jF^2{}_{\text{obsd}}}$$

and

$$R_2 = \frac{\sum\limits_u \left(\sum\limits_g jF^2{}_{\text{obsd}} - \sum\limits_g jF^2{}_{\text{calcd}} \right)^2}{\sum\limits_u \left(\sum\limits_g jF^2{}_{\text{obsd}} \right)^2}$$

and where j is the multiplicity factor. The symbol $\sum\limits_g$ represents the sum over a group of reflections which are not resolvable to individual reflections and $\sum\limits_u$ represents a sum over the u independent measurements. Minimization of R_2 is directly related to the steepest descents[10] and the least squares methods[11] in the structure refinement, while in general R_1 has a parallel relation to R_2. In Fig. 2, both R_1- and R_2-curves give a well-defined minimum at the C–C distance of 1.28 ± 0.03 Å. corresponding to $z = 0.403 \pm 0.002$. In the powder diffraction method, if the structure has a few parameters to be determined, the diagrammatical

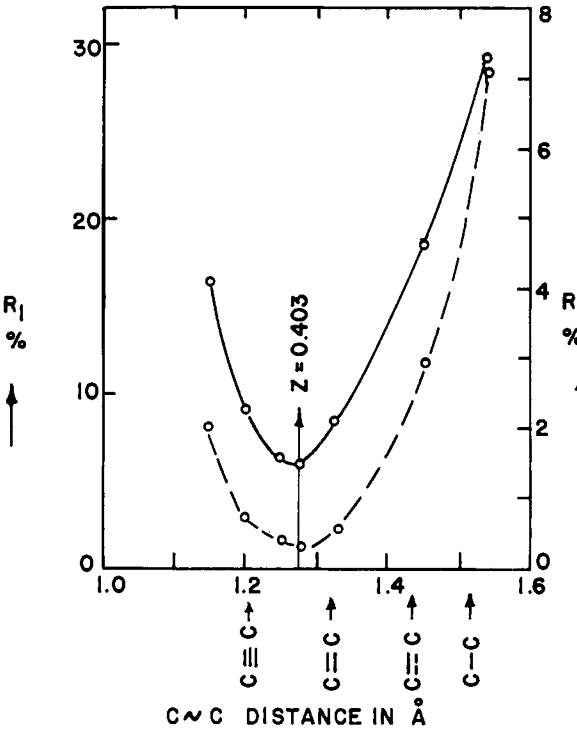

Fig. 2.—Parameter determination for LaC_2: R_1 and R_2 values as percentages are shown as solid and dashed lines, respectively. Single, conjugated, double and triple bond C–C distances are indicated below the ordinate.

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(6) F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, "Crystal Stuctures of Some of the Rare Earth Carbides," to be published.

(7) G. E. Bacon, "Neutron Diffraction," Oxford, 1955, p. 90.

(8) W. C. Koehler and E. O. Wollan, *Phys. Rev.*, **91**, 597 (1953).

(9) C. G. Shull and E. O. Wollan, *ibid.*, **81**, 527 (1951).

(10) A. D. Booth, *Nature*, **160**, 196 (1947).

(11) D. P. Shoemaker, J. Donohue, V. Schomaker and R. B. Corey, THIS JOURNAL, **72**, 2328 (1950).

use of R-space is very effective and is much less laborious than the usual computational methods.

On the other hand, the algebraic solutions obtained from six pairs of the isolated or well-formed peaks, such as (312) and (303), gave consistently $z = 0.403 \pm 0.002$. In Table I, the calculated values with $z = 0.403$ are listed together with the observed data. The temperature factor, $\exp(-0.6 (\sin\theta/\lambda)^2)$, was obtained by minimizing the R-factors, and has been applied to all calculated F^2-values. The final R_1 and R_2 factors are 0.061 and 0.0034, respectively. The reflections with $\sin \theta/\lambda > 0.51$ Å.$^{-1}$ have been omitted because the experimental error is quite large owing to overlapping of the peaks.

Table I

Observed and Calculated Neutron Diffraction Intensities

Indices	jF^2_{obsd}	$jF^2_{\text{calcd}}\, e^{-0.6(\sin \theta/\lambda)^2}$	Indices	F^2_{obsd}	$jF^2_{\text{calcd}}\, e^{-0.6(\sin \theta/\lambda)^2}$
		(1) LaC_2[a]			
101	<4	2			
002	15	13	301, 222	53	2, 48
110	92	73	204	278	1
112	47	51	105, 310		134, 134
200	71	71	312	103	95
103	39	42	303	41	39
211	45	4	006	<8	1
202		50	321	10	4
004	<2	0	224	253	1
114	153	1	215		257
220		69	116	<10	3
213		80			
		(2) La_2C_3[a]			
211	45	28	444	100	115
220	<16	10	710, 543	260	197, 95
310	259	247	640	500	26
321	300	306	721, 633		252, 238
400	140	132	642	280	227
420	20	29	730	161	172
332	145	130	732, 651	400	122, 266
422	70	53	800		14
510, 431	370	72, 297	741	460	250
521	<10	8	820		165
440	67	91	653		57
530	100	82	822, 660	410	26, 8
611, 532	130	146, 7	831, 750, 743		43, 3, 214
620	185	187	752		127
541	120	161	840		0
631	320	308			

[a] The units of F^2 are 10^{-24} cm.^{2} and 10^{-23} cm.^{2} for LaC_2 and La_2C_3, respectively.

Lanthanum Sesquicarbide

X-Ray Results.—The lattice constant of La_2C_3 depends upon composition, varying from 8.803 ± 0.003 Å. at 56.2 atomic % carbon to 8.819 ± 0.003 Å. at 60.2 atomic % carbon; at the ideal composition (60 atomic %) it is 8.817 ± 0.003 Å. Carbon content was determined by change in weight of the carbide upon ignition in oxygen at 900°, and the analyses are reproducible to ± 0.05%. The X-ray density of La_2C_3 is 6.079 which is in reasonable agreement with the pycnometric density of 5.992 g./cm.^{3}.

The observed reflections verify previous work.[2,3] The systematic absences are: (a) h,k,l is absent if $h + k + l = 2n + 1$, (b) h,k,l is absent if h,k,l are all even and $h + k + l = 4n + 2$, and (c) h,h,l is absent if $2h + l = 4n + 2$. Conditions (a) and (c) uniquely determine the space group to be T_d^6-$I\bar{4}3d$. From X-ray work alone it is possible that only the metal positions conform to this group, but the neutron diffraction data yield no exceptions to (a) and (c), so that the space group is confirmed. From condition (b) the sixteen lanthanum atoms per unit cell must be placed on threefold axes, in positions 16(c), at (xxx), etc.

Intensity data from X-ray powder diagrams were obtained by visual comparison of films with timed exposures of 2, 4, 8 and 16 hours. A trial and error fit of the x-parameter to the observed intensities of the last 13 powder lines yielded a value of $x = 0.053 \pm 0.003$, in good agreement with the result for Pu_2C_3 ($x = 0.050 \pm 0.003$).[3] More quantitative neutron data confirm this value and establish it within narrower limits.

It is noteworthy that this phase exists for all of the rare earths examined (Eu and Pm were not examined) up to and including Ho, but not for the higher rare earths.[6]

Neutron Diffraction Results.—The lanthanum sesquicarbide used contained LaC_2 and cubic lanthanum metal (β-La)[12] as impurities, and the data had to be corrected for these impurities. Fortunately, the (002), (112) and (200) reflections of LaC_2 could be isolated from others in the neutron-diffraction diagram (Fig. 3). After all LaC_2 peaks were subtracted, the (111) peak of β-La was isolated. Since the neutron-diffraction diagram of β-La was not available, the calculated diffraction peaks were obtained in the following manner.

A Gaussian type of peak shape was assumed

$$I(2\theta) = \frac{I_0 h}{\sqrt{\pi}} \exp(-4h^2(\theta - \theta_0)^2)$$

where I_0 is the integrated intensity and θ_0 is the Bragg angle. The half-width at half-height for the normalized peak is defined by

$$\theta_h = \frac{0.8325}{h}$$

where θ_h is independent of I_0, but is dependent upon θ; the half width is expressed in terms of the reflection angle, 2θ. θ_h was obtained from the LaC_2 pattern and is shown as a function of 2θ in Fig. 4. θ_h is almost constant for small values of 2θ, but at large values it increases exponentially. This feature can be interpreted in terms of the instrumental function and of the mosaic distributions in crystals.[13] At small values of 2θ, θ_h increases very gradually as 2θ decreases, for reasons as yet unknown. Nevertheless, we may assume that the β-La diffraction diagram has the same θ_h variations as those obtained from LaC_2.

The temperature factor for β-La was estimated as $\exp(-0.92(\sin\theta/\lambda)^2)$ for F, using the Debye temperature 162°K.[14] and the formula based on

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(12) E. Zintl and S. Neumayr, *Z. Elektrochem.*, **39**, 84 (1933).

(13) C. E. Bacon, "Neutron Diffraction," Oxford Press, New York, N. Y., 1955, p. 95.

(14) The Debye temperature for La, θ_D = 123 to 137°K., has been reported by Spedding, Legvold, Daane and Jennings in C. J. Gorter,

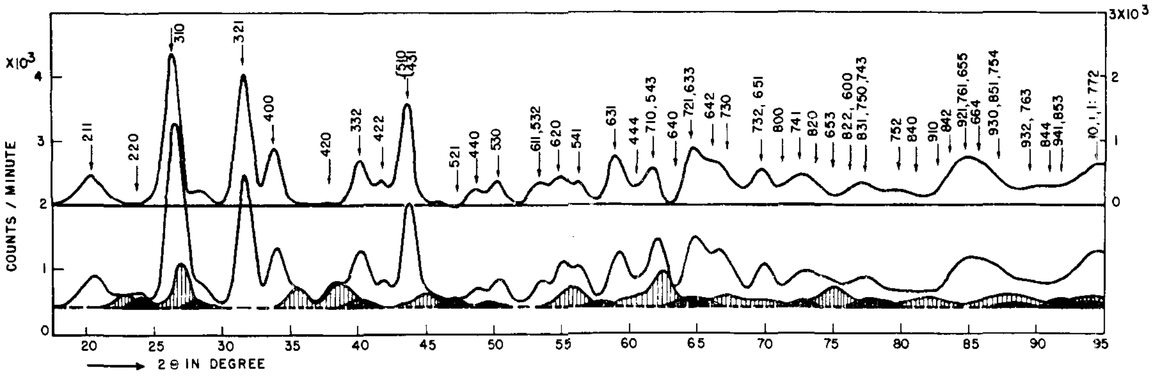

Fig. 3.—Neutron scattering curve for La_2C_3. In the lower half of the figure the open curve is the experimental curve which includes impurities. The peaks with vertical lines and the shaded peaks are the computed peaks due to LaC_2 and β-La impurities, respectively. The upper curve is the corrected diffraction curve for La_2C_3, for subtracting out the LaC_2 and β-La contributions to the experimental curve.

Debye's theory.[15] The diffraction peaks of β-La were then calculated and were subtracted from the experimental diffraction pattern. Reasonable neutron-diffraction curves for La_2C_3 were thus obtained.

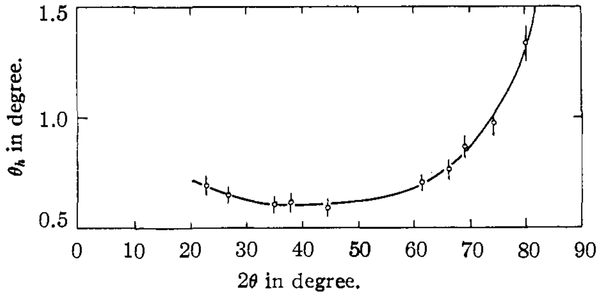

Fig. 4.—The half-width at the half-height of the peaks in LaC_2 diffraction pattern.

The space group, $T_d^6 - I\bar{4}3d$, obtained by the X-ray method,[2,3] was confirmed by neutron diffraction. After the trial and error treatment it was also confirmed that lanthanum atoms and carbon atoms occupy the positions with C_3-3 and C_2-2 point symmetry, respectively.[16] The two dimensional R_1- and R_2-contours (Fig. 5) gave the parameters $x = 0.053 \pm 0.001$ in (xxx) for La, and $y = 0.300 \pm 0.002$ in $(y\ 0\ {}^1/_4)$ for C. The temperature factor, $\exp(-1.3(\sin\theta/\lambda)^2)$, was applied to all calculated F^2-values. The final R_1 and R_2 factors for the reflections within $\sin\theta/\lambda = 0.51$ Å.$^{-1}$ are 0.073 and 0.0058, respectively. The observed and calculated values are listed in Table I.

Elliptical R_2-contours, as in Fig. 4, have been discussed extensively by Quarashi[17] in connection with the optimum conditions for convergence of steepest descents. It is of interest that R_1-contours have similar scaling representation to R_2's, but show relatively less curvature than R_2's. Moreover, the R_2-contours are more circularly symmetric. Therefore, the use of R_2-space is more advantageous for refining the parameters than the use of R_1-space. This has been pointed out vaguely and implicitly by many authors, but Fig. 4 shows explicitly this aspect.

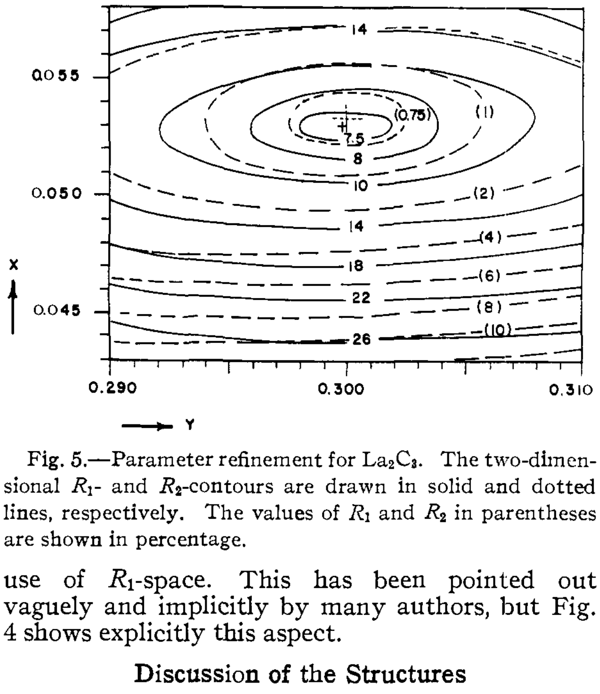

Fig. 5.—Parameter refinement for La_2C_3. The two-dimensional R_1- and R_2-contours are drawn in solid and dotted lines, respectively. The values of R_1 and R_2 in parentheses are shown in percentage.

Discussion of the Structures

LaC_2 is metallic with a conductivity comparable to that of lanthanum metal.[5] CaC_2, on the contrary, is an ionic crystal and insulator.[18] Since the structures are very similar it is apparent that the difference must lie in the valences of lanthanum and calcium. Calcium is divalent and CaC_2 has properties suggesting that it is a true salt, $Ca^{++}C_2^{=}$. True stable salts of La^{++} are unknown, and LaC_2 probably can be described approximately in terms of $La^{+3}C_2^{=}$, with the extra electron in a conduction band. Indeed, it is reported that LaC_2 and CaC_2 are mutually soluble over an extensive composition range, with metallic conduction in this range and varying colors as in the sodium tungsten bronzes (Na_xWO_3).[18] In the bronzes the conductivity

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"Progress in Low Temperature Physics," Vol. II, 1957, North-Holland, Amsterdam, p. 374. Differences between the reported θ_D-values are not very significant in our calculations. These θ_D's are for hexagonal La metal. It is not unlikely that cubic La metal has a value of θ_D close to the one for hexagonal La metal.

(15) R. W. James, "The Optical Principles of the Diffraction of X-Rays," Bell, London, 1950, p. 223.

(16) "International Tables for X-Ray Crystallography," Kynoch, 1952, p. 329.

(17) M. M. Quarashi, *Acta Cryst.*, **2**, 404 (1949).

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

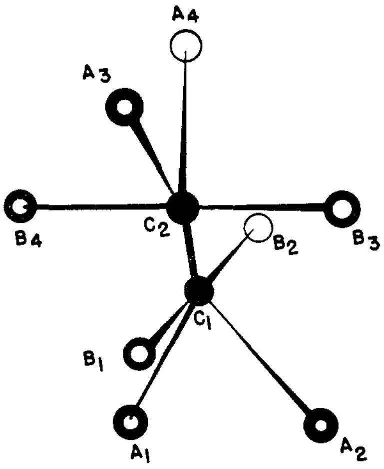

Fig. 6.--Configuration about C_2 group in La_2C_3. A and B represent La atoms. The bond distances are: C_1–A_1 = 2.83 Å.; C_1–B_1 = 2.71; C_1–B_3 = 3.01; A_1–A_2 = 3.60; A_2–B_1 = 3.81; A_1–B_1 = 4.04; A_1–B_4 = 3.60; B_1–B_4 = 4.04.

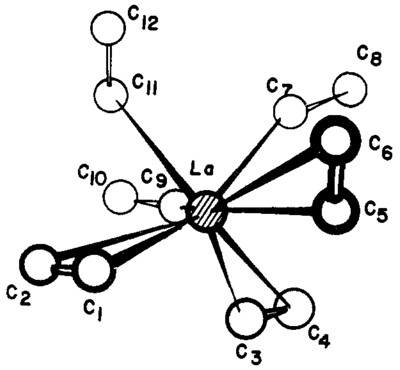

Fig. 7.--Configuration of the C_2 groups about an La atom in La_2C_3. The bond distances are: La–C_1,C_3,C_5 = 2.71 Å.; La–C_2,C_4,C_6 = 3.01; La–C_7,C_9,C_{11} = 2.83. C–C nonbonded distances fall into two groups 3.5 and 4.8 Å.

has been shown to approximate closely the predictions of free electron theory, and from conductivity and Hall coefficient measurements the carriers have been shown to be electrons equal in number to the number of sodium atoms in the formula above.[19] Hence it is attractive to suggest that one electron per lanthanum in $La_xCa_{1-x}C_2$ is contributed to a conduction band.

La_2C_3 also contains C_2 groups or ions and also is a metallic conductor,[5] though its conductivity is only about half that of lanthanum metal or the dicarbide. Here, if $C_2^=$ ions are formed and the extra lanthanum valence electrons are contributed to a conduction band, the ratio of conducting electrons to $C_2^=$ ions is 2 rather than 1 as in LaC_2.

It is interesting that the C_2 distance is larger in La_2C_3 than in LaC_2, since it might be expected that the C_2 groups or ions partially capture the valence electrons of lanthanum. If they capture these up to $C_2^=$ the electrons are expected to be bonding electrons, leading to a triple bond, :C≡C:, corresponding to an electronic state for an isolated $C_2^=$ ion of $K^2K^2\sigma_s^2\sigma^*{}_s^2\sigma_p^2\pi^4$. Any additional electrons would have to go into π^*-antibonding levels and should lengthen the C–C distance. If this is correct, CaC_2 should have a shorter C–C distance than LaC_2, and La_2C_3 should have a longer one as observed; solid solutions of CaC_2 and LaC_2 should have intermediate distances depending upon composition. Likewise, dicarbides of tetravalent metals, such as ThC_2[20] and UC_2 should have C–C distances as long as those in La_2C_3.

The reported C–C distance in CaC_2 is 1.4 Å., but is probably too inexact to test this hypothesis. The C–C distances in dicarbides of tetravalent metals also are not known precisely. Clearly these and solid solutions of LaC_2 and CaC_2 deserve further study.

If one wishes to adopt a more covalent view of these carbides, and use Pauling's empirical rules relating distances to bond numbers, the results are rather satisfactory in that C and La then have calculated valences near the expected values of 4 and 3, respectively (Table II).

Table II

Interatomic Distances and Bond Numbers

		LaC_2			
C–C	1.28 Å.	n = 2.73	La–2C	2.65 Å.	n = 0.48
C–La	2.65 Å.	n = 0.48	La–8C	2.85 Å.	n = 0.22
C–4La	2.85 Å.	n = 0.22	La–4La	3.93 Å.	n = 0.12
		Σn for C = 4.11			
		Σn for La = 3.24			
		La_2C_3			
C–C	1.32 Å.	n = 2.34	La–3La	3.60 Å.	n = 0.43
C–2La	2.71 Å.	n = 0.38	La–3C	2.71 Å.	n = 0.38
C–2La	2.83 Å.	n = 0.24	La–3C	2.83 Å.	n = 0.24
C–2La	3.01 Å.	n = 0.12	La–3C	3.01 Å.	n = 0.12
		Σn for C = 3.83			
		Σn for La = 3.53			

Thus in LaC_2, the C_2 group appears to be acetylene-like with one nearest lanthanum at 2.65 Å. from the carbon on a line colinear with the C–C bond. Four other lanthanum atoms sit around the C_2 group as though π-bonded to it. Bond numbers, distances and coördination numbers are given in Table II for this carbide.

The configuration of lanthanum atoms about C_2 groups in La_2C_3 is illustrated in Fig. 6. The point symmetry of the mid-point of the C_2 group is S_4-$\bar{4}$, and approximates D_{2d}-$\bar{4}m2$. Referring to Fig. 6, ∠ $A_1C_1A_2$ is 79.1°, while ∠ $B_1C_1B_2$ is 180°. The angle between A_1A_2 and B_1B_2 is 84.9°. Distances are given in the legend of Fig. 6.

The configuration of the C_2 groups about a lanthanum atom (point symmetry C_3-3) is shown in Fig. 7. It is to be noted from Table II that each lanthanum atom also has three nearest lanthanum neighbors at only 3.60 Å., compared with 3.75 Å. for nearest neighbors in β-La. Other distances are given in the legend of Fig. 7.

Acknowledgment.—The authors are greatly indebted to Dr. S. Sidhu of Argonne National Laboratory for making it possible for us to use the neutron diffraction equipment at Argonne National Laboratory and for his advice during the course of the neutron diffraction investigation.

Ames, Iowa

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(19) W. R. Gardner and G. C. Danielson, *Phys. Rev.*, **93**, 43 (1954).

(20) E. B. Hunt and R. E. Rundle, This Journal, **73**, 4777 (1951).