I. INTRODUCTION

Superconductivity in binary rare earth carbides has been an intensively investigated topic for many years. Outstanding in this family of compounds with respect to their superconducting transition temperatures $T_c$ are the sesquicarbides $\text{RE}_2\text{C}_3$, RE being the nonmagnetic rare earth metals Y and La. These systems recently regained attention due to the finding by Amano et al. and Nakane et al. who reported the successful synthesis of binary $\text{Y}_2\text{C}_3$ under high pressure conditions ($\sim$5 GPa). They reported transition temperatures $T_c$ and critical fields $B_{c2}$ of 18 K and $>30$ T, respectively.\(^{\text{1,2}}\)

All RE carbides of composition $\text{RE}_2\text{C}_3$ are isotypic; they crystallize in the cubic $\text{Pu}_2\text{C}_3$ structure-type (see Fig. 1). Electronic structure calculations, based on the $\text{Pu}_2\text{C}_3$ structure type, have been carried out recently for $\text{Y}_2\text{C}_3$ by Shein et al. and by Singh and Mazin.\(^{\text{3,4}}\) Singh and Mazin specifically discuss the origin and magnitude of the electron-phonon coupling in $\text{Y}_2\text{C}_3$. They identify low-frequency metal atom vibrations to have the largest coupling whereas the contribution of the high-frequency C–C stretching vibrations is found to be comparatively small.

So far, the samples of $\text{Y}_2\text{C}_3$ showing a $T_c$ of 18 K have been characterized by x-ray powder diffraction only. A more detailed investigation of these phases with respect to the exact composition and the phase diagram is still pending. In this respect $\text{La}_2\text{C}_3$, which shows superconductivity with $T_c$ up to 13.2 K and which can be prepared at ambient pressure, is better understood.\(^{\text{5,6}}\)

We report here the equation of state and the effect of pressure on the structure of $\text{La}_2\text{C}_3$. The structural properties were measured up to 30 GPa using synchrotron powder x-ray diffraction in the angle-dispersive mode. Our primary motivation was to investigate how pressure affects the structural degrees of freedom of the $\text{Pu}_2\text{C}_3$-type phase; these are thought to play a key role in controlling the details of the electronic structure in the vicinity of the Fermi level. Second, the equation of state and phase stability of $\text{La}_2\text{C}_3$ is of interest in the context of pressure synthesis of rare earth carbides. To our knowledge, pressure-dependent studies similar to the ones presented here have not been reported so far for any of the known rare earth and actinide sesquicarbides.

II. SAMPLE CHARACTERIZATION, DIFFRACTION EXPERIMENTS

The superconducting properties of $\text{La}_2\text{C}_3$ depend sensitively on the carbon content. Spedding et al. and Gschneidner et al. report a homogeneity regime for $\text{La}_2\text{C}_{3-x}$ which ranges from 56.2 at.-% to 60.2 at.-% carbon with cubic lattice parameters from 8.803 Å to 8.818 Å, respectively.\(^{\text{7,8}}\) Recently, Simon and Gulden reinvestigated the phase diagram of $\text{La}_2\text{C}_{3-x}$ ($0 < x < 0.33$).\(^{\text{8}}\) They find that the boundary phases with $x = 0$ and $x = 0.33$ are homogeneous but that by sufficiently extended annealing, samples within the homogeneity range tend to phase separate into the boundary phases with $x = 0$ and $x = 0.33$. According to magnetic susceptibility measurements these boundary phases have sharp

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**FIG. 1:** (Color online) The $\text{Pu}_2\text{C}_3$-type cubic crystal structure of $\text{La}_2\text{C}_3$ [space group (SG) $\text{Fm} \text{d}$ (No. 220), $Z = 8$ formula units in the cubic cell]. The dicarbide anions occupy the voids in bisphenoids of the metal substructure. Note: Different from the standard crystallographic setting, the origin of the indicated unit cell is shifted into a La position.
superconducting transitions at 5.6 K and at 13.2 K, respectively. The latter value obtained for the stoichiometric phase La$_2$C$_3$ is appreciably increased over the early $T_c$ of 11 K reported by Giorgi et al.\textsuperscript{10,11} The 13.2 K phase shows critical fields $B_{c2} \geq 17$ T, significantly enhanced over $B_{c2} = 12$ T found by Francavilla et al.\textsuperscript{12} (see also Ref. 13).

The polycrystalline sample of La$_2$C$_3$ used in the present study was prepared by arc melting appropriate quantities of La metal (Alfa, 99.99%) and graphite chips (Deutsche Carbone, 99.99%) with a slight excess (2 to 3%) of graphite. The graphite chips had been heated (1050 °C) and degassed in vacuum ($10^{-5}$ mbar) for one day and then stored in a dried argon atmosphere. The sample pellets were annealed at 650 °C for 3 days and cooled to room temperature at a rate of 10 °C/hr. All subsequent sample manipulations, including preparations for pressure experiments, were done in dry argon atmosphere.

The phase composition was checked by laboratory-based powder x-ray diffraction measurements using Cu Kα$_1$ radiation; these showed La$_2$C$_3$ as the majority phase (~85%) with a lattice parameter of 8.8150(6) Å. Weak additional reflections were observed which are attributed to an impurity phase of tetragonal LaC$_2$ ($a=3.9323(6)$ Å, $c=6.574(1)$ Å), its overall fraction being less than ~15%. The superconducting properties of the sample were determined by resistivity, magnetic susceptibility, and heat capacity measurements. The resistive transition (midpoint) and the onset of diamagnetic shielding occurs at $T_{\text{onset}} = 13.5(1)$ K (see Fig. 2). The width of the resistive transition (10%-90% criterion) amounts to 0.1 K. The heat capacity proves bulk superconductivity with a characteristic anomaly at $T_c$ of $\Delta C_p/\gamma T_c \approx 2.2$; the deviation from the standard BCS anomaly is most likely due to enhanced electron-phonon coupling.

Figure 3 shows representative diffraction diagrams of La$_2$C$_3$ collected at 5 and 15 GPa. The cubic phase was observed up to the highest pressure of this study, 30.7 GPa, and after releasing pressure. Extra Bragg reflections seen in the diffraction diagrams are consistent with the presence of tetragonal LaC$_2$ (SG...
The diffraction patterns were analyzed by the Rietveld method using the program GSAS. The refined parameters for the sesquicarbide phase (space group $I\overline{4}3d$) were the lattice constant, the fractional coordinate $(x, x, x)$ of the 16c (La) site, a common isotropic thermal parameter for all atom sites, a Chebyshev polynomial background, Pseudo-Voigt profile function parameters, and an overall intensity scaling factor. The refinements were not sensitive to the exact value of the positional parameter $v$, 0, 0.25 of the carbon 24d site. Hence, $v$ was fixed at 0.3049 (Ref. 18), corresponding to a C–C distance of 1.236 Å at ambient and assumed independent of pressure. A preferred orientation correction was applied, but was found to result in only minor improvements of the refinements. Two-phase refinements were performed in order to account for the admixture of tetragonal $LaC_2$, but only the unit cell parameters were refined for this phase; its internal parameter for the carbon position was assumed constant ($z=0.4024^{18}$, corresponding to a C–C distance of 1.284 Å at ambient). Figure 3 illustrates the results of the refinements for the two patterns collected at 5.0 and 15.0 GPa. The convergence was achieved at residuals (with a subtracted background) $R_{wp} = 8.7\%$ for 5 GPa and at $R_{wp} = 8.2\%$ for 15 GPa.

The experimental pressure-volume data of $LaC_3$ are shown in Fig. 4. At 30 GPa, $LaC_3$ is compressed by 18% and the volume is comparable to that of $Y_2C_3$ at ambient conditions. The pressure-volume data were fitted by a Birch equation of state:

$$P(x) = \frac{3}{2}B_0 \cdot [x^{-7} - x^{-5}] \times \left[1 - \frac{3}{4}(B'_0 - 4)(1 - x^{-2})\right],$$

where $x = (V/V_0)^{1/3}$ is a reduced length. The parameters are the volume $V_0$, the bulk modulus $B_0$, and its pressure derivative $B'_0$, all at zero pressure. The fitted parameters and their standard deviations are given in Table II. The obtained value for $V_0$ is consistent with literature data.

Among the sesquicarbide compounds with the cubic $Pu_2C_3$-type structure, $LaC_3$ has the largest lattice parameter and therefore is expected to represent the most compressible candidate in this family of compounds.

There appears to be no experimental data available on the bulk moduli of other cubic rare earth sesquicarbides to compare with. The bulk modulus of $LaC_3$ at 30 GPa is about 250 GPa. This value would be an upper limit for the ambient-pressure bulk modulus $B_0$ of $Y_2C_3$: it is much lower than the calculated one ($B_0 = 363$ GPa) reported in Ref. 18.

At ambient conditions, the volume per $LaC_3$ formula unit (85.68 Å³) is smaller than that of the constituents La metal and carbon in the diamond modification (La metal 37.5 Å³/La, diamond 5.67 Å³/C, $2 \times 37.5 + 3 \times 5.67 = 92.0$ Å³). So, the $P\Delta V$ term in the free energy difference favors the formation of the compound under pressure. However, because of the large compressibility of La metal ($B_0$ (La) $\approx 25$ GPa, Ref. 21), the $P\Delta V$ term changes sign at about 5 GPa (Fig. 4). Hence, $LaC_3$ is not necessarily a thermodynamically stable phase at all pressures covered in our experiment. A high-temperature experiment performed above 5 GPa may result in decomposition or, perhaps, the formation of a metal-rich carbide.

The $Pu_2C_3$-type structure is closely related to the anti-Th$_3$P$_4$-type. This similarity becomes obvious when writing the stoichiometry as $La_4(C_2)_3$ instead of $LaC_3$. The metal atoms in the $Pu_2C_3$ structure form a 3D network...
of condensed RE₅ bisphenoids. The dicarbide anions are centered at the interstitial 12a site (3/8, 0, 1/4) and oriented along the \( \overline{4} \) axes of the bisphenoids (Fig. 1) whose shape depends on the positional parameter \( x \). For \( La_2C_3 \) we have \( x(La) \approx 0.05 \) which is intermediate between nearly equal lengths of all edges (\( x \approx 1/32 \)) and equal center-corner distances (\( x = 1/12 \)). Near \( x = 0.05 \) the metal-metal coordination is \( 3 + 2 + 6 \) and the bisphenoids can host elongated entities.

Within the uncertainty of our data, the positional parameter \( x(La) \) stays constant under pressure (Fig. 4). This means that the coordination polyhedron around \( C_2 \) is compressed isotropically, and there is no change in the second neighbor coordination. Actually, at ambient pressure the \( x \) parameters of all cubic rare earth and actinide sesquicarabides cluster around 0.051 with a quite narrow spread of \( \pm 0.002 \). The arrangement of metal ions in \( La_2C_3 \) is similar to that of the ‘c116’ (16-atom body centered cubic) phase of high-pressure Li which can be interpreted as a \( 2 \times 2 \times 2 \) superstructure of bcc. In Li-c116 a pseudo-gap is formed, involving a lowering of the density of states \( N(E_F) \) at the Fermi level, which leads to a decrease of the total energy relative to any of the common high-symmetry phases of elemental metals. Despite the pseudo-gap formation, the c116 phase of Li is a superconductor with \( T_C \geq 10 \) K (see Ref. 23 and literature cited therein). As for \( La_2C_3 \), the Fermi level is calculated to also fall into a local minimum of the DOS. This is qualitatively similar to what is reported for \( Y_2C_3 \). It is not clear whether the formation of a local DOS minimum in the sesquicarbides is a consequence of the structural distortion of the metal sublattice away from bcc. In any case, the states in the DOS minimum of \( Y_2C_3 \) show a strong coupling to ‘symmetry-preserving’ metal atom displacements, i.e. a change in the \( x \) parameter.

For \( La_2C_3 \), a C–C distance of 1.236 Å is given in Ref. 3. A slightly larger distance, about 1.29 Å (Ref. 3), appears more plausible. Unfortunately, our experiments do not provide any information on the pressure dependence of the C–C distance. This distance will correlate with the degree of charge transfer between \( La \) and antibonding (\( \pi^* \)) states of the \( C_2 \) unit. We can expect that the back-donation effect increases with pressure.

We now turn to \( LaC_2 \), the impurity phase in our sample. \( LaC_2 \) crystallizes in a body-centered tetragonal structure (Fig. 3). The \( C_2 \) units in \( LaC_2 \) (C–C distance 1.28 Å) are reported to be oriented parallel to the \( c \) axis, \( 12 \) and \( 25 \); they are sixfold coordinated by La atoms which form elongated octahedra.

The pressure-volume data of \( LaC_2 \) are shown in Fig. 6. Parameters obtained by fitting a Birch relation to the high-pressure data are given in Table I. The back-extrapolated zero pressure volume given in Table I is 0.3% larger than \( V_0 = 102.0 \) Å\(^3\) measured after pressure cycling. The latter value agrees with Ref. 14. Despite the larger carbon to metal ratio, the bulk modulus of \( LaC_2 \) comes out slightly lower compared to \( La_2C_3 \). This may be explained by the larger metal-metal distance in \( LaC_2 \) (12 \( \times \) 3.93 Å at ambient pressure) compared to the average value for \( La_2C_3 \) (5 \( \times \) 3.63 Å, 2 \( \times \) 3.81 Å, 6 \( \times \) 4.01 Å). The inset of Fig. 6 illustrates that the \( c/a \) ratio of \( LaC_2 \) increases with increasing pressure, i.e., the compressibility is smaller along the direction of the dumbbell orientation.

The diffraction pattern of \( LaC_2 \) was completely lost at pressures above 13 GPa, but it reappeared upon releasing pressure. It is left to a separate study to find out whether \( LaC_2 \) undergoes a reversible pressure-induced phase transition. Already at ambient pressure, the volume of \( LaC_2 \) is larger than that of the constituents (\( LaC_2 = 51 \) Å\(^3\) per formula unit at \( P = 0, La + 2 C = 48.84 \) Å\(^3\)). So, application of pressure should be a strong driving force for a phase change, not ruling out at this point a pressure-induced amorphization as a precursor to phase separation. Another question, brought up by studies of \( CaC_2 \)
at ambient pressure, concerns the orientation of the C\textsubscript{2} dumbbells in tetragonal LaC\textsubscript{2}. Our data point to a possible c/a anomaly near ambient pressure (see inset of Fig. 8) which could be related to a pressure-dependent reorientation.

In conclusion, the present high-pressure structural study gives quantitative information on the equation of state and structural parameters of superconducting La\textsubscript{2}C\textsubscript{3}. The results may serve as a reference for the as yet unknown high-pressure behavior of other cubic rare earth sesquicarbides. The results are also believed to provide useful input for modelling the pressure-dependence of the electronic structure and the electron-phonon coupling of La\textsubscript{2}C\textsubscript{3}.

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