Strong electron-phonon coupling in the rare-earth carbide superconductor La$_2$C$_3$

J. S. Kim, W.-H. Xie, R. K. Kremer, V. Babizhetskyy, O. Jepsen, and A. Simon
Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany

K. S. Ahn
Department of Chemistry, Yonsei University, Wonju 220-710, South Korea

B. Raquet, H. Rakoto, and J.-M. Broto
Laboratoire National des Champs Magnétiques Pulsés, 143 avenue de Rangueil, 31432 Toulouse, France

B. Ouladdiaf
Institute Laue-Langevin, Grenoble, Cedex 9, France

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We present the results of a crystal structure determination using neutron powder diffraction as well as the superconducting properties of the rare-earth sesquicarbide La$_2$C$_3$ ($T_c \approx 13.4$ K) by means of specific heat and upper critical field measurements. From the detailed analysis of the specific heat and a comparison with *ab-initio* electronic structure calculations, a quantitative estimate of the electron-phonon coupling strength and the logarithmic average phonon frequency is made. The electron-phonon coupling constant is determined to $\lambda_{ph} \approx 1.35$. The electron-phonon coupling to low energy phonon modes is found to be the leading mechanism for the superconductivity. Our results suggest that La$_2$C$_3$ is in the strong coupling regime, and the relevant phonon modes are La-related rather than C-C stretching modes. The upper critical field shows a clear enhancement with respect to the Werthamer-Helfand-Hohenberg prediction, consistent with strong electron-phonon coupling. Possible effects on the superconducting properties due to the non-centrosymmetry of the crystal structure are discussed.

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I. INTRODUCTION

The recent discovery of superconductivity in MgB$_2$ and alkaline earth-intercalated graphites as well as Li at high pressures has renewed the interest in electron-phonon (e-ph) coupled superconductors without strong electron-electron correlations. The electronic states and phonon modes relevant for superconductivity vary from system to system, but in general superconductivity in these compounds benefits from the light atomic mass of constituents e.g. of boron, carbon and lithium. When a specific part of the Fermi surface (FS) couples strongly to high frequency phonon modes, an increase of $T_c$ can be achieved even if the e-ph coupling averaged over the full FS remains moderate. This mechanism opens a new route to achieve high $T_c$’s by e-ph pairing. This is often associated as the “metallic hydrogen superconductivity” scenario.

The rare earth sesquicarbides, $R_2$C$_3$ ($R =$ Rare earths), which crystallize in the bcc Pu$_2$C$_3$ structure-type, have been suggested as possible candidates, in which such conditions are realized. Early on, $T_c$ of La$_2$C$_3$ and Y$_2$C$_3$ was found to be $\sim$ 11 K, and Th doping in Y$_2$C$_3$ raises $T_c$ to 17 K, comparable with the $T_c$’s of the A15 compounds. In the Pu$_2$C$_3$ structure, C$_2$ dumbbells are located inside the rare earth metal atom cage. Since the C-C bond is quite short, the phonon frequency for the C-C stretching phonon modes is expected to be very high. In fact, recent *ab-initio* calculations showed that the C-C stretching phonon frequency in Y$_2$C$_3$ is $\sim$1442 cm$^{-1}$. Therefore e-ph coupling between the high frequency phonons and C-C antibonding states at the Fermi level ($E_F$) has been considered as an origin of the relatively high $T_c$ in Y$_2$C$_3$ and La$_2$C$_3$.

Superconductivity in rare earth sesquicarbides recently regained attention because of the discovery of 18 K superconductivity in Y$_2$C$_3$ samples prepared under high pressure ($\sim$ 5 GPa). The upper critical field ($H_{c2}$) is also significantly increased and amounts to $H_{c2}(0) >$30 T. Electronic structure calculations for Y$_2$C$_3$, however, demonstrated that the high frequency C-C bond stretching phonon modes contribute less than 10% of the total e-ph coupling, and rather low frequency Y(-C) phonons must be considered to be the relevant modes for superconductivity. For stoichiometric band filling, the e-ph coupling constant $\lambda_{ph}$ is predicted to be $\approx$ 0.6. These results were consistent with previous $H_{c2}$ studies on La$_2$C$_3$, which reported $\lambda_{ph} \sim$ 0.8 suggesting moderate e-ph coupling. However, such a moderate e-ph coupling appears to be too small to generate the relatively high $T_c$ in the sesquicaride superconductors. Therefore, to reconcile with the measured $T_c$, it is necessary to consider either significant e-ph coupling with the high frequency C-C stretching phonon modes or strong e-ph coupling with the low frequency rare earth related phonon modes. In order to shed light on this controversy, further exper-
perimental studies on the superconducting properties of the $R_2C_3$ are required.

In this paper we focus on one of the rare earth sesquicarbides, La$_2$C$_3$. We investigate its superconducting properties together with the crystal and electronic structures. In the rare earth sesquicarbides, it has been well known that $T_c$ as well as the structural properties vary significantly depending on the synthesis and annealing conditions, essentially due to C deficiency. Therefore in order to carry out reliable studies on such compounds, one needs to characterize the superconducting properties simultaneously with the structural properties with particular attention to C deficiency. Unlike Y$_2$C$_3$, which requires high pressure and high temperature preparation, La$_2$C$_3$ can be prepared at ambient pressure conditions using standard arc melting technique, and larger sample quantities can easily be synthesized. Recently, we reported that $T_c$ of La$_2$C$_3$ can be enhanced up to 13.4 K using excess C in the starting composition of the materials combined with an adequate post-annealing.

In addition, La$_2$C$_3$ can be a potential system for investigating the effect of non-centrosymmetry in the structure. The space group symmetry of $R_2C_3$, $I43d$, belongs to the tetrahedral crystallographic class $T_d$ lacking a center of symmetry. When the crystal structure has no center of symmetry and spin-orbit coupling is significant, the degenerate spin-up and spin-down bands are mixed and split, which can induce unexpected superconducting properties. For example, one of the well-known non-centrosymmetric superconductors CePt$_3$Si (where Ce $f$-bands possess significant spin-orbit coupling) shows unconventional superconducting properties such as high $H_{c2}(0)$ exceeding the Pauli limit and a line node in the superconducting order parameter. However, this system also shows a heavy fermion nature, and it is not clear yet how far the origin of the exotic properties has to be attributed to the non-centrosymmetry. Thus, it is required to explore other non-centrosymmetric superconductors without strong electron correlations. In this respect, $R_2C_3$ compounds with non-magnetic rare earths, can also be such model compounds to study only the effect of the non-centrosymmetric structure without the interference from the magnetism of the constituents.

In case of Y$_2$C$_3$, the spin-orbit coupling for Y $d$-bands may be rather small, thus we can not expect a significant effect of non-centrosymmetry. Because of the higher atomic mass of La as compared to Y, spin-orbit coupling effects in La$_2$C$_3$ is expected to be more pronounced than in Y$_2$C$_3$. Note that La is placed next to Ce in the periodic table and accordingly is expected to generate comparable spin-orbit coupling.

The paper is organized as follows: we first provide experimental details including a brief description on the synthesis procedures (Sec. II). Secondly we discuss the crystal structure at low temperatures gained from neutron powder diffraction (NPD) investigations (Sec. III) and report the electronic structures of La$_2$C$_3$ obtained from ab-initio calculations (Sec. IV). Specific heat (Sec. V) and the upper critical fields (Sec. VI) on the samples characterized by NPD are presented. Finally we will discuss the $e$-$ph$ coupling strength of La$_2$C$_3$ and also the effects of non-centrosymmetry on the superconducting properties (Sec. VII).

II. EXPERIMENTAL

Polycrystalline samples of La$_2$C$_3$ were synthesized by arc melting the constituents on a water-cooled Cu crucible under purified Ar atmosphere. La metal chips (Ames Laboratory, 99.99%) were used with spectroscopic grade graphite chips (Deutsche Carbone, 99.99%). Before use, the graphite chips were outgased overnight at 950 °C under high vacuum conditions ($P < 10^{-5}$ mbar). The starting materials were melted more than 6 times and at each time the button was turned over to ensure homogeneity. La$_2$C$_3$ is very moisture-sensitive, tending to decompose readily within a few minutes on exposure to the air. Consequently all handling of the starting materials and the samples after synthesis was performed in an Ar filled glove box (M. Braun $P_{H_2O} < 0.1$ ppm).

It has been reported that a homogeneity range exists for La$_2$C$_3$ extending from 45.2% to 60.2% atom-% C content. After investigation of a series of La$_2$C$_3$–$x$ samples, it was concluded that samples with a carbon deficit upon annealing phase separate into two superconducting phases with rather sharp $T_c$ ’s of ~6 K and 13.4 K. The latter transition which can be attributed to the almost stoichiometric La$_2$C$_3$ phase, is significantly higher than the $T_c$ of ~11 K reported so far for La$_2$C$_3$. Therefore, to obtain samples with a single sharp superconducting transition at 13.4 K, it is essential to compensate possible losses of C in the arc melting and the subsequent annealing procedure by an excess of carbon up to 10%, although this may result in the impurity phase which is identified to be LaC$_2$. Heat treatment of the sample buttons was performed in sealed Ta tubes under purified Ar atmosphere at 1000°C. After annealing at high temperatures, the samples were slowly cooled to room temperature with a rate of 5°C/hour.

Neutron powder diffraction experiments on 2 samples of La$_2$C$_3$ (samples, S1 and S2, cf. Table I) were performed at room temperature using the GEM diffractometer at the ISIS laboratory. For low temperature neutron powder experiments, another La$_2$C$_3$ sample (sample S3) of $\approx 10$ g was sealed into a vanadium can under 1 bar of He gas and measured down to 5 K on the D2B diffractometer at the Institut Laue-Langevin (ILL). The structural parameters as well as the La$_2$C$_3$/LaC$_2$ composition were gained from two-phase Rietveld refinements using the FULLPROF package. $T_c$ was determined from dc magnetic susceptibility measurements using a SQUID magnetometer (Quantum Design, MPMS XL magnetometer). The specific heat ($C_p$) was measured using a PPMS calorimeter (Quantum Design) employing the relaxation method. The $C_p$ contribution from the
La$_2$C$_3$ impurity phase was estimated from the results of a separate run on a pure LaC$_2$ sample characterized also with neutron powder diffraction. To determine the upper critical fields, we measured the temperature dependence of the resistivity for a bar shape sample (1 $\times$ 1 $\times$ 5 mm$^3$) of La$_2$C$_3$ at different magnetic fields up to 11 T. For magnetic fields higher than 11 T, we performed magnetization and resistivity measurements in a pulsed magnetic field up to 30 T at the Laboratoire National des Champs Magnétiques Pulsés in Toulouse.

III. NEUTRON POWDER DIFFRACTION

La$_2$C$_3$ crystallizes with the cubic Pu$_2$C$_3$ structure (I43d) with 8 formula units in the unit cell. As shown in Fig. 1 C-C dumbbells are located in a distorted dodecahedral coordination ('bisphenoid') formed by 8 La atoms. So far, several crystal structure determinations for La$_2$C$_3$ have been carried out by neutron powder diffraction and also by x-ray single crystal diffraction. Some variation found for the lattice parameters ranging from $a = 8.804$ to 8.818 Å at room temperature. Such a wide spread of structural parameters has been already known for Y$_2$C$_3$ as well as other C-containing superconductors like MgCNi$_3$. It is related to the C content and often affects the superconducting properties quite substantially. For example, in MgC$_2$Ni$_3$, the density of state at $E_F$, $N(E_F)$, decreases rather abruptly due to disorder-induced smearing of the electronic bands. In addition, $e$-$ph$ coupling mostly due to the low energy Ni-dominated phonon modes is reduced by C deficiency. Similar effects of C deficiency may also cause the large variations of superconducting properties in R$_2$C$_3$ compounds.

Figure 1 shows the neutron powder diffraction patterns of La$_2$C$_3$ (S3) collected at $T = 300$ K and 5 K. In addition to the reflections which can be ascribed to La$_2$C$_3$, there are extra weak reflections, which belong to the impurity phase, identified as LaC$_2$ (I4/mmm). A two-phase Rietveld refinement was preformed to account for the admixture of the La$_2$C$_3$ phase whose weight fraction is refined to $\approx 18\%$. The converged parameters of the La$_2$C$_3$ phase include the lattice constants, the fractional coordinates ($u$, $v$, $w$)$_{La}$ of the La 16c site and ($v$, 0, 1/4)$_{C}$ of the C 24d sites, an isotropic (anisotropic) thermal parameters for the La (C) sites. After refinements with the aforementioned parameters, in a last step, the C occupancy was varied. We checked convergence by varying the C occupancy in the cases where the other refined parameters are fixed or relaxed. For both cases, a C deficiency of $\sim 2\%$ is derived consistently. The results of the refinements for the two patterns collected at $T = 300$ K - 5 K are listed in Table I. Also the results for samples S1 and S2 obtained using time-of-flight (TOF) patterns collected at room temperature are given.

The C-C distance at room temperature amounts to $\approx 1.295$ Å, in agreement with the previously reported value, 1.296(9) Å [Ref. 27] but smaller than that reported early on, 1.32 Å. Similar C-C distances have also been observed in binary rare earth dicarbides and ternary carbide halides. From the studies of electronic behavior on a series of the dicarbides, MC$_2$, the C-C bond length inside the octahedral metal atom cage is found to be linked to the valence state of the M atoms. In a simple ionic picture, CaC$_2$ (Ca$^{2+}$)$_2$ with filled bonding $\pi$ states but empty antibonding $\pi^*$ states, has a short C-C bond distance of $\approx 1.2$ Å, while with increasing electron count for the C$_2$ unit e.g. in UC$_2$ (U$^{4+}$)$_2$($\pi^*$), the C-C bond distance increases to $\approx 1.35$ Å as the antibonding $\pi^*$ states are gradually filled. La$_2$C$_3$ has a shorter C-C bond in a C$_2$($\pi^*$) unit, which is presumably due to the different degree of charge transfer to antibonding C-C $\pi^*$ states. These results indicate that the charge transfer between $M$ states and antibonding $\pi^*$ state of the C-C dimers strongly depends not only on the valence state of $M$, but also the local environment around the C-C dimers because of different cage structure.

Interestingly we observed a significant temperature dependence of the C atom position in contrast to that of the metal atom cage which contracts in a regular way. With decreasing temperature a slight increase of the C-C bond distance is found (see Table I). A possible explanation of this observation could be a temperature dependence...
TABLE I: Structural parameters for La$_2$C$_3$ obtained from Rietveld refinements of neutron powder diffraction patterns at $T = 300$ K (S1-S3) and at low temperature down to 5 K (S3). $a$ is the cubic lattice parameter and $d_{C-C}$ is the C-C bond length. $u$ and $v$ are the fractional coordinates of the La 16c site ($u$, $u$, $u$)$_{La}$ and the C 24d sites ($v$, 0, 1/4)$_{C}$, respectively. The reduced $\chi^2$, the occupancy for C are listed. The employed method, time-of-flight (TOF) and constant-wavelength (CW) neutron powder diffraction is also indicated.

| Sample | $T$ (K) | $a$ (Å) | $u$ (La) | $v$ (C) | $\chi^2$ | $d_{C-C}$ (Å) | C occupancy | Method |
|--------|--------|--------|---------|--------|---------|--------------|-------------|--------|
| S1     | 300    | 8.8091(8) | 0.05255(3) | 0.30155(9) | 2.074  | 1.2942(16) | 0.983(8)   | TOF    |
| S2     | 300    | 8.8090(1)  | 0.05268(6) | 0.30171(16) | 1.325  | 1.2911(28) | 0.977(5)   | TOF    |
| S3     | 300    | 8.8096(3)  | 0.05255(6) | 0.30144(14) | 8.96   | 1.2977(19) | 0.982(2)   | CW     |
|        | 200    | 8.8013(3)  | 0.05251(5) | 0.30085(13) | 9.42   | 1.3001(17) | CW         |
|        | 100    | 8.7936(3)  | 0.05251(5) | 0.30085(13) | 10.06  | 1.3041(17) | CW         |
|        | 5      | 8.7904(3)  | 0.05250(5) | 0.30065(13) | 10.29  | 1.3071(17) | CW         |

of the charge transfer between the C-C $\pi^*$ to the La $d$ states. A carbon-metal orbital overlap will be affected by volume contraction at low temperatures, which will modulate the charge transfer between La $d$ and C-C $\pi^*$ states. Another possible origin could be a tilting motion of the C-C dimers leading to unusual non-elliptical temperature factors which can not be accounted for by the refinement procedure. Further studies are ongoing to clarify this issue.

IV. ELECTRONIC STRUCTURE CALCULATIONS

The electronic structure of La$_2$C$_3$ has been studied using the full-potential linear augmented plane wave (LAPW) method with local orbital extension, within the generalized gradient approximation (GGA). We performed total-energy calculations for a series of the lattice parameters. For each lattice parameter the internal parameters (atomic positions) were relaxed according to the atomic forces. By this procedure, the fully relaxed structural parameters have been obtained including the lattice constant as well as the La and C atomic positions. The calculated equilibrium lattice constant is $a = 8.829$ Å, with a C-C distance of 1.333 Å and a La-C distance of 2.709 Å, corresponding to internal parameters, $u_{La} = 0.0524$ and $v_{C} = 0.2995$. In comparison with the Rietveld refinement results at 5 K, the calculated lattice parameter is within the normal error bar of LAPW calculations ($\sim 1\%$), while the internal atomic parameters for both La and C are in good agreement.

Figure 2 displays the electronic structure with and without spin-orbit coupling included, using the optimized structural parameters. There are 6 C-C dimers in the primitive cell, and the orbitals on these form bonding and antibonding C-C $\pi-\pi^*$ bands. The C 2s derived bands extend from -15.6 eV to -6.2 eV, relative to the Fermi energy. The lowest bands around -14 eV and the bands around -7.5 eV are the bonding and antibonding states, respectively. The bands around -4 eV are the bonding carbon $p$ bands. The bands crossing the Fermi level, separated by a 2.5 eV gap from the bonding C-C $\pi$ bands, are the hybridized La $d$ and C-C antibonding $\pi^*$ states.

FIG. 2: Upper panel: Calculated band structure of La$_2$C$_3$ with spin-orbit coupling, using the theoretical lattice constant with fully relaxed atomic positions. For comparison, the band structures near $E_F$ with (middle panel) and without (bottom panel) spin-orbit coupling are also presented.
The electronic structure obtained including spin-orbit coupling is quite similar to that without spin-orbit coupling, except that the number of bands is doubled due to the asymmetric spin-orbit coupling effect (See middle and bottom panels in Fig. 2). Lacking inversion symmetry in the structure along with significant spin-orbit coupling, some spin-up and spin-down bands are mixed and the degeneracy is lifted. Therefore, in contrast to the previous conjecture\cite{Singh2013,Cao2014}, the band splittings due to the asymmetric spin-orbit coupling do exist, and may also affect the superconducting properties. In particular, for La$_2$C$_3$, relatively flat bands are crossing $E_F$, thus such a band splitting may alter significantly the total electronic density of states (DOS) at $E_F$. In Fig. 3 we show the DOS with and without spin-orbit coupling around $E_F$. The DOS near the Fermi level is characterized by a broad minimum centered at about 50 meV below $E_F$. In Fig. 3 we show the DOS with and without spin-orbit coupling around $E_F$. As shown in the inset of Fig. 3 for stoichiometric compounds $N(E_F)$ is reduced by $\sim 10\%$ by introducing the spin-orbit coupling.

We also calculated the DOS for the system with 2\% C deficiency by employing the virtual-crystal approximation. We noticed a shift of peaks towards higher energies above $E_F$. As seen in Fig. 3 while the electronic structure based on the stoichiometric sample puts $E_F$ on the shoulder of the peak located near the Fermi level, $E_F$ for the 2\% C deficient sample lies close to a minimum. This leads to a reduction of $N(E_F)$ by $\sim 25\%$ as compared to the DOS based on the stoichiometric La$_2$C$_3$ assuming no spin-orbit coupling. Introducing the spin-orbit coupling, the reduction of $N(E_F)$ is even more pronounced and amounts to $\sim 30\%$. Thus slight C deficiency can significantly change the electronic properties. This provides an explanation of the strong dependence of $T_c$ and the upper critical field on the composition found in Y$_2$C$_3$ and La$_2$C$_3$\cite{Cao2014,oras2014,oras2015,Bourianoff2015}.

Singh and Mazin concluded that $\lambda_{ph}$ has a maximum at the stoichiometric band filling\cite{Singh2013}. This is closely related to the observation that the Fermi energy falls on a peak in the electronic density of states. Hence, $T_c \approx 13.4\ K$ in the present 2\% C deficient La$_2$C$_3$ samples is already higher than the previously known $T_c \sim 11\ K$, but it seems that there is still a possibility to increase $T_c$ further for stoichiometric La$_2$C$_3$. In this view, the doping dependence of $T_c$ for La$_2$C$_3$ can also be understood. Th doping in La$_2$C$_3$ enhances $T_c$ up to 14.3 K\cite{Singh2013} while Lu or Y doping slightly decreases $T_c$.\cite{Singh2013} Considering the electron count for Th, Th doping at the La sites will donate more electrons than La, in contrast to Y or Lu substitution. For the previously investigated La$_2$C$_3$ samples ($T_c \sim 11\ K$), the reduced electron concentration due to C deficiency, is compensated by Th doping, but not by Lu or Y doping. Therefore, enhancement of $T_c$ by Th doping can be attributed to the recovery of the band filling towards the stoichiometric value.

V. SPECIFIC HEAT

Figure 4 shows the temperature dependence of the specific heat of La$_2$C$_3$ (S1) at $H = 0$ and $H = 9\ T$. The contribution of LaC$_2$ to the total sample capacity, which amounts to $\lesssim 5\%$ over the whole temperature range, was subtracted. Note that $T_c$ of LaC$_2$ is $\lesssim 1.6\ K$\cite{Singh2013} below the temperature range of the present measurements. There is no offset of $C_p/T$ at $H = 0$ as the temperature approaches zero as can be seen in the inset of Fig. 4. This proves that the $C_p$ contribution from the non-superconducting part, LaC$_2$ has been completely accounted for the subtraction. A sharp anomaly at $\approx 13.4\ K$ is clearly resolved indicating bulk superconductivity in the La$_2$C$_3$ sample, which has not been observed before.
The onset of 13.4 K determined from the specific heat jump is consistent with that obtained from the susceptibility measurements. At \( H = 9 \) T, the superconducting anomaly is shifted to lower temperatures. A clear deviation from a Debye \( T^3 \) law is observed in the normal state \( C_p \), which can be attributed to a contribution from low-lying Einstein phonon modes.

In order to account for the normal state \( C_p \), we fitted the data obtained at \( H = 9 \) T by a polynomial,

\[
C_p(T) = \gamma_N T + C_{\text{lattice}}(T) = \gamma_N T + \beta T^3 + \delta T^4. \tag{1}
\]

Here, \( \gamma_N \) is the Sommerfeld coefficient and \( \beta \) is related to the Debye temperature \( \Theta_D(0) \) via

\[
\Theta_D^3(0) [K] = 1944 n / \beta [J/molK^4], \tag{2}
\]

where \( n \) is the number of atoms per formula unit. Since the applied magnetic field \( H = 9 \) T is not sufficient to suppress superconductivity completely, we used a constraint according to

\[
\int_0^{T_c} C_p(T) / T \, dT = \int_0^{T_c} (\gamma_N + \beta T^2 + \delta T^4) \, dT, \tag{3}
\]

to assure the entropy conservation for the superconducting state.

The solid line in Fig. 5 is the best fit to the \( H = 9 \) T data for \( T_c(H = 9 \) T) \(< T < 15 \) K, yielding the parameters, \( \gamma_N = 10.60(4) \) mJ/mol K\(^2 \), \( \beta = 228.2(11) \) \( \mu \)J/mol K\(^4 \), and \( \delta = 0.5988 \) \( \mu \)J/mol K\(^5 \). The measured \( \gamma_N \) is much higher and more realistic than those previously reported from specific heat and upper critical fields measurements. The corresponding Debye temperature \( \Theta_D(0) = 349(1) \) K is comparable with that found in previous work.

The specific heat difference \( \Delta C_p(T)/T \) between the normal and superconducting state and the entropy for the superconducting state is shown in Fig. 5. For comparison, we also plot the BCS curve for the weak \( e\text{-}ph \) coupling limit. A clear deviation from the BCS curve is observed. The \( C_p \) anomaly at \( T_c \) as well as the intersection temperature where \( \Delta C_p(T)/T = 0 \) is much higher than expected from the BCS prediction. The solid (red) line is the theoretical fit based on the ‘\( \alpha \)-model’ assuming an isotropic \( s \)-wave BCS gap \( \Delta(T) \) scaled by the adjustable parameter, \( \alpha = \Delta(0) / k_B T_c \). For the weak coupling limit \( \alpha \) is 1.76. The detailed temperature dependence of \( \Delta C_p(T)/T \) was fitted by two adjustable parameters: \( \alpha \) and the Sommerfeld coefficient \( \gamma_N \). The data are very well reproduced by \( \alpha = 2.43 \) and \( \gamma_N = 8.97 \) mJ/mol K\(^2 \). The \( \gamma_N \) value from the \( \alpha \) model fit is slightly smaller than obtained from the normal state \( C_p \), but in view of the experimental resolution and the accuracy of the model, it can be considered as satisfactory agreement. The normalized specific heat jump, \( \Delta C_p / \gamma_N T_c \) is also higher than the weak limit BCS value, 1.426 giving a clear indication for an enhanced \( e\text{-}ph \) coupling.

The normalized electronic specific heat, \( C_{es}/\gamma_N T_c \) in the superconducting state is shown in Fig. 6. The solid line is an exponential fit to the data for \( 2.0 \leq T_c/T_c \leq 4.5 \) using the form \( C_{es}/\gamma_N T_c \propto \exp(-0.82 \alpha T_c/T) \) with \( \alpha = 2.31(5) \). \( C_{es} \) exponentially vanishes for \( T \to 0 \) K, clearly manifesting the absence of gap nodes in the superconducting order parameter. The \( \alpha \) value is somewhat lower than found from the \( \alpha \)-model fit in which the ratio \( \Delta(0)/k_B T_c \) is largely determined by the shape of the

![FIG. 5: (Color online) Superconducting part of the electronic specific heat. The (red) solid line is the best fit according to the \( \alpha \)-model assuming an isotropic \( s \)-wave BCS gap as described in the text. The (blue) dashed line represents the BCS result. The inset shows the entropy conservation for the electronic specific heat in the superconducting state.](image)

![FIG. 6: (Color online) The electronic contribution of the specific heat \( C_{es} \) is plotted on a logarithmic scale versus \( T_c/T \). The (red) straight line is an exponential fit for \( 2.0 \leq T_c/T \leq 4.5 \). The magnetic field dependence of Sommerfeld coefficient \( \gamma(H) \) is presented in the inset with the dashed line as a guide to the eye.](image)
$C_p$ jump near $T_c$. However the discrepancy is less than 10%, which is probably due to a restricted temperature range. The magnetic field dependence of $\gamma(H)$ at $T \rightarrow 0$ K is estimated from the linear fit of $C_p/T$ versus $T^2$ for $2 \text{ K} \leq T \leq 4 \text{ K}$, and it is found to increase linearly with $H$ for low fields up to $H \approx 0.4 \text{ H}_c$. This behavior consistently supports a fully-gapped and almost isotropic superconducting order parameter.\(^{22}\)

The thermodynamic critical field $H_c(T)$ can be determined using $H_c(T) = \sqrt{-8\pi\Delta F}$ where $\Delta F$ is the free energy extracted from the specific heat in the superconducting state, $\Delta C_p = -T d^2(\Delta F)/dT^2$. The temperature dependence of $H_c(T)$ is shown in Fig. 8. Based on the BCS theory, $H_c(0)$ is derived from a fit to the temperature dependence of $H_c(T)$ for $T \rightarrow 0$ which is given by

$$\left(\frac{H_c(T)}{H_c(0)}\right)^2 = 1 - 2.12\beta \left(\frac{T}{T_c}\right)^2,$$

where the empirical parameter $\beta$ is $\sim 1$ for the weak coupling limit but reduced with increasing $e$-ph coupling. The solid line in Fig. 8 is a best fit yielding $H_c(0) = 151.3(1) \text{ mT}$ and $\beta = 0.7933(3)$ indicating as well strong $e$-ph coupling. The deviation function, $D(t) = H_c(T)/H_c(0)-(1-t^2)$ with $t = T/T_c$ as well provides clear signatures for strong $e$-ph coupling. In the case of strongly $e$-ph coupled superconductors, $D(t)$ is positive and shows a broad maximum while the weak-coupling BCS curve exhibits a negative dip at $t^2 \approx 0.5$. As shown in the inset of Fig. 8, $D(t)$ for La$_2$C$_3$ passes through a maximum at $t^2 \approx 0.5$.

Based on the specific heat results for the superconducting states, we conclude that La$_2$C$_3$ is an $s$-wave, single gap superconductor with strong $e$-ph coupling. Recently, Harada et al. from $^{13}$C nuclear-magnetic-resonance measurements suggested a multi-gap superconductivity for Y$_2$C$_3$. Since the Fermi surface consists of several sheets from hybridized La $d$ and $C\ p$ states, we cannot rule out such a possibility for La$_2$C$_3$ as well. However, as shown above, the specific heat for the superconducting state can be well explained in terms of a single superconducting gap. Usually, in a system where the $d$ bands are hybridized with $s$ or $p$ bands, the disparity between the bands is reduced, and impurity scattering significantly smears out the two-gap superconductivity.\(^{29,20}\) Considering the polycrystalline nature of the sample, therefore, it is rather unlikely that, if any, two-gap superconductivity survives. Further studies are required to clarify the possible two-gap superconductivity in the sesquicarbide systems.

![FIG. 7: (Color online) The temperature dependence of the thermodynamic critical field $H_c(T)$ estimated from the specific heat in the superconducting state. The solid (red) line is a best fit (see the text). The inset shows the deviation function, $D(t) = H_c(T)/H_c(0)-(1-t^2)$ with $t^2 = (T/T_c)^2$. The weak coupling BCS curve is also presented for comparison.](image)

### VI. UPPER CRITICAL FIELDS

Figure 8(a) shows the temperature dependence of the resistivity under different magnetic fields up to $H = 11$ T. $T_c$ is determined at 50% decrease from the normal state resistivity value and the transition width is taken as the temperature interval between 10% and 90% of the transition. In order to determine $H_{c2}(T)$ at low temperatures,
the magnetoresistance was measured up to \( \approx 30 \) T at different temperatures from \( T = 1.8 \) to 10 K (Fig. 8(b)). The transition width remains almost unchanged down to low temperatures. As a consistency check we also carried out high field magnetization measurements at low temperatures. \( H_{c2}(T) \) is determined as a kink of the first derivative of \( M(H) \) (See the inset of Fig. 8).

The \( H_{c2}(T) \) data obtained from the three different methods are compiled in Fig. 9. For comparison, we plotted the Werthammer-Helfand-Hohenberg (WHH) prediction for conventional superconductors. There is a clear deviation from the WHH behavior in the \( H_{c2}(T) \) curve. This is in contrast to the previous report on the \( H_{c2}(T) \) of \( \text{La}_2\text{C}_3 \) sample (\( T_c \sim 11 \) K), which followed the WHH prediction rather well. Such an enhancement of \( H_{c2}(T) \) has been attributed to several different origins such as localization effects in highly disordered superconductors and strong \( e-ph \) coupling of the Fermi surface. First, considering disorder effects, the application of the magnetic field weakens the localization effects and thus reduces the Coulomb pseudopotential \( (\mu^*) \). This in turn strengthens the superconductivity and leads to an enhancement of \( H_{c2} \) as the temperature decreases and larger fields have to be applied to drive the system into the normal state. Therefore, the enhancement of \( H_{c2} \) is closely linked to the negative magnetoresistance in the normal state. The positive magnetoresistance observed in \( \text{La}_2\text{C}_3 \) (See Fig. 8), however, indicates that the localization effects tend to be enhanced under high magnetic fields, which rules out the possibility of disorder-induced enhancement of \( H_{c2} \). Secondly, when the FS is distorted from the spherical shape, an increase of \( H_{c2} \) becomes more pronounced due to an anisotropy in the FS shape. Electron structure calculations for \( \text{La}_2\text{C}_3 \) unveil rather complex multisheets of the Fermi surface, similar to that of \( \text{Y}_2\text{C}_3 \) (cf. Fig. 5 in Ref. [5]). A quantitative comparison between experiment and theory is beyond the scope of this work, but considering the distorted FS shape, the FS anisotropy will most likely contribute to the enhancement of \( H_{c2} \) at low temperatures. Note, however, that the previous report on \( H_{c2}(T) \) for \( \text{La}_2\text{C}_3 \) (\( T_c \sim 11 \) K) with C deficiency showed good agreement with the WHH curve. With C deficiency, the detailed FS can be modified, but the overall FS shape would be preserved, thus similar enhancement of \( H_{c2} \) at low temperatures is expected even for C-deficient samples with lower \( T_c \). Therefore it seems that the FS anisotropy cannot be the only source for \( H_{c2} \) enhancement. Another possibility is strong \( e-ph \) coupling. When the \( e-ph \) coupling is in the strong coupling regime \( (\lambda_{ph} > 1) \), \( H_{c2}(T) \) starts to deviate from the WHH curve and remains linear down to lower temperatures showing finally an upward curvature for higher \( e-ph \) coupling. As shown in Fig. 8(b), \( H_{c2}(T) \) for \( \text{La}_2\text{C}_3 \) shows an almost linear temperature dependence down to \( \approx 0.2T_c \). From the specific heat studies, we already found evidence that the \( e-ph \) coupling is in the strong coupling regime, thus it will also affect the temperature dependence of \( H_{c2} \) for \( \text{La}_2\text{C}_3 \).

From an extrapolation, we obtained \( H_{c2}(0) \approx 19 \) T. Even though \( H_{c2}(0) \) is much more enhanced than the WHH prediction, it is still clearly below the Pauli limit of \( H_p = \Delta(0)/2\sqrt{2}U_B = 1.83 \) k\( \nu^* \)T\( _c \approx 24.5 \) T for the weak coupling limit. Considering the strong \( e-ph \) coupling with enhanced \( \Delta(0)/k_B T_c = 2.31 - 2.43 \), \( H_p(0) \) can be even higher up to \( \approx 32 \) T. Therefore, \( H_{c2}(0) \approx 19 \) T, well below the Pauli limit, indicates that \( H_{c2} \) is mainly determined by orbital depairing under magnetic fields. This result suggests that the possible effect due to noncentrosymmetry is not significant for \( H_{c2} \) as we will discuss below (see Sec. VII).

Based on the \( H_{c2}(0) \) and \( H_c(0) \) values, we estimated the superconducting parameters for \( \text{La}_2\text{C}_3 \). According to the Ginzburg-Landau (GL) theory, the upper critical field \( H_{c2}(0) \), the lower critical field \( H_{c1}(0) \) and the thermodynamic critical field \( H_c(0) \) can be described with the GL coherence length \( \xi(0) \) and the GL parameter \( \kappa(0) = \lambda(0)/\xi(0) \) according to

\[
H_{c2}(0) = \frac{\Phi_0}{2\pi \xi(0)}.
\]

\[
H_{c1}(0) = \frac{H_{c2}^2(0)}{H_{c2}(0)} [\ln \kappa(0) + 0.08],
\]

\[
H_c(0) = \frac{H_{c2}(0)}{\sqrt{2\kappa(0)}},
\]

where \( \Phi_0 \) is the flux quantum. With \( H_{c2}(0) = 19 \) T and \( H_c(0) = 151 \) mT, we obtained \( \xi(0) \approx 42 \) Å and \( \lambda(0) = 373 \)

![FIG. 9: (Color online) The temperature dependence of the upper critical field for \( \text{La}_2\text{C}_3 \) samples, S1 (square) and S3 (circle), estimated from \( \rho(H) \) (filled symbols), \( M(H) \) (crossed symbols), and \( \rho(T) \) (open symbols) measurements. For comparison, the Werthammer-Helfand-Hohenberg curve with the Maki parameter \( \alpha = 0 \) and the spin-orbit scattering \( \lambda_{SO} = 0 \) (see Ref. [5]) is presented with (blue) dashed line. The Pauli limit \( H_p \) is indicated by the arrow.](image-url)
position temperature is much smaller for La
II. In Li
other non-centrosymmetric superconductors (See Table
measurements using muon-spin-rotation experiments.
conventional BCS type behavior with the isotropic super-
parameters. Furthermore, it has been suggested that
description of the superconducting properties should at
least include two bands due to the non-centrosymmetry in rare earth sesquicarbides. Our electronic structure
calculations confirm the splitting in the electronic bands
near \( E_F \) indicating that the spin degeneracy is lifted due
to the sizable asymmetric spin-orbit coupling.

However, even though \( H_{c2}(0) \) is clearly enhanced, it
does not exceed the paramagnetic limit (Fig. 9). The
specific heat at low temperatures also reveals that the
superconducting gap in \( \text{La}_2\text{C}_3 \) has an isotropic s-wave sym-
metry. Therefore the effect of the non-centrosymmetry
appears to be not significant in \( \text{La}_2\text{C}_3 \). Note that the
band splitting with respect to the superconducting trans-
tion temperature is much smaller for \( \text{La}_2\text{C}_3 \) than in
other non-centrosymmetric superconductors (See Table 
III). In \( \text{Li}_4\text{Pd}_3\text{B} \) where the band splitting due to non-
centrosymmetry is comparable with that of \( \text{La}_2\text{C}_3 \),
conventional BCS type behavior with the isotropic super-
conducting gap has been found from penetration depth
measurements using muon-spin-rotation experiments. Therefore for \( \text{La}_2\text{C}_3 \), the asymmetric spin-orbit coupling
appears to be not strong enough to induce a significant
effect on the superconducting properties. In this respect,
it would be very interesting to study heavier rare earth
metal carbides such as \( \text{Lu}_2\text{C}_3 \) (\( T_c \approx 15 \text{ K} \)) and \( \text{Th}_2\text{C}_3 \)
(\( T_c \approx 4 \text{ K} \)).

For e-ph coupled superconductors, Carbotta has pro-
posed that the characteristic thermodynamic quantities
follow empirical formulas which can be described by one
adjustable parameter, \( x = \omega_n/T_c \) where \( \omega_n \) is the loga-
TABLE II: Energy splitting of the bands at \( E_F \) (\( \Delta E \)) and \( T_c \)
for several non-centrosymmetric superconductors.
\[
\begin{array}{|c|c|c|c|c|}
\hline
\text{Material} & \Delta E \text{ (meV)} & \Delta E/k_B T_c & T_c \text{ (K)} & \text{Ref.} \\
\hline
\text{La}_2\text{C}_3 & 20 - 30 & \sim 20 & 13.4 & \text{this work} \\
\text{CePt}_3\text{Si} & 50 - 200 & > 1000 & 0.75 & 19 \\
\text{Cd}_2\text{Pt}_2\text{O}_7 & \sim 70 & \sim 700 & \sim 1 & 57 \\
\text{Li}_2\text{Pt}_3\text{B} & \sim 200 & > 1000 & \sim 2 & 58 \\
\text{Li}_2\text{Pd}_3\text{B} & 20 - 50 & > 35 - 85 & \sim 7 & 58 \\
\hline
\end{array}
\]

\[
\frac{2\Delta(0)}{k_B T_c} = 3.53 \left[ 1 + 12.5x^{-2}\ln \frac{x}{2} \right],
\]
\[
\frac{\Delta C_p(T_c)}{\gamma N T_c} = 1.43 \left[ 1 + 53x^{-2}\ln \frac{x}{3} \right],
\]
\[
\frac{\Delta C_p(T) - \Delta C_p(T_c)}{\gamma N T_c - \gamma N T} = -3.77 \left[ 1 + 117x^{-2}\ln \frac{x}{2.9} \right],
\]
\[
\frac{\gamma N T_c^2}{H_c(0)} = 0.168 \left[ 1 - 12.2x^{-2}\ln \frac{x}{3} \right],
\]
\[
\frac{H_c(0)}{dH_c(T)/dT \mid_{T_c}} = 0.576 \left[ 1 - 13.4x^{-2}\ln \frac{x}{3.5} \right].
\]

This analysis has been successfully applied to various
metal-alloy superconductors, and also to other re-
cently discovered carbon-contained superconductors such as
borocarbides and MgNi_3.

Figure 10 shows the thermodynamic quantities with
variation of \( x = \omega_n/T_c \) according to Eqs. (8)-(12).
measured values extracted from the $C_p$ data are also plotted onto the empirical curves. Each thermodynamic quantity provide a value for $x = \omega_{in}/T_c$ as indicated for three La$_2$C$_3$ samples (S1-S3) in Fig. 11. From five $x$'s and $T_c = 13.4$ K, we obtain a mean value $\omega_{in} = 109$ K ± 24 K, 101 K ± 24 K, and 121 K ± 32 K for the sample S1, S2, and S3, respectively. Averaging all $\omega_{in}$'s for the samples we conclude on $\omega_{in} = 110$ K ± 27 K. This $\omega_{in}$ value is only ~30% of the Debye temperature, $\omega_D$ ≈ 350 K. The Debye frequency is determined only from the phonon DOS profile, $F(\omega)$, while $\omega_{in}$ results from a weighting by the e-ph coupling function $\alpha^2(\omega)$. Such a reduced $\omega_{in}$ value compared to $\omega_D$ indicates the importance of the low energy phonon modes for the superconductivity. The deviation of the normal state $C_p$ from the Debye $T^3$ law (See, Fig 11) supports the presence of the low-lying Einstein phonon modes.

From ab-initio calculations for Y$_2$C$_3$, the frequencies of the full symmetry Raman modes are estimated to be 175 cm$^{-1}$ for a Y dominated mode and 1442 cm$^{-1}$ for an almost pure C-C bond stretching mode. The relevant phonon modes for the superconductivity, therefore, are the La dominated phonon modes rather than the high frequency C-C bond stretching modes. From simple conversion based on the atomic mass difference between La and Y, we can estimate the frequency of the La dominated Raman mode to be ~140 cm$^{-1}$. In comparison with $\omega_{in} = 76$ cm$^{-1}$ ± 15 cm$^{-1}$, this phonon frequency is somewhat higher. However, since the lattice constant of La$_2$C$_3$ is larger than that of Y$_2$C$_3$, the interatomic forces are expected to be somewhat weaker for La$_2$C$_3$. The estimated frequency of the La dominated phonon mode, therefore, is rather overestimated, and it can be reduced and come closer to the $\omega_{in}$. Recent ab-initio calculations for Y$_2$C$_3$ also reported that most of the e-ph coupling emerges from the low frequency Y related phonon modes, not from the high frequency C-C phonon modes.

Other relevant phonon modes for superconductivity in La$_2$C$_3$ could be the tilting vibrations of the C-C dimer. For AC$_2$ ($A = Ca$, Sr, and Ba) containing the C-C dimers inside the octahedral metal atom cage, it has been shown that the binding of the C-C dimer to the surrounding octahedral metal atom cage is weak, thus allowing a structural transition from tetragonal to a cubic phase at high temperatures as well as several modifications of the C-C dimer structure at low temperatures. Raman scattering studies on rare-earth carbide halides also showed that the frequency of the C-C tilting modes is ~400 cm$^{-1}$, much lower than the stretching modes with a frequency of ~1590 cm$^{-1}$. Compared to the octahedral metal atom cages, the size of a bisphenoid La cage is larger, thus the binding of the C-C dimer to the La cage could be even weaker. Consequently the tilting modes of the C-C dimer in La$_2$C$_3$ are expected to have lower frequencies, which can allow sizable contribution to e-ph coupling. Further studies on the C-C dimer tilting modes e.g. Raman scattering experiments or ab-initio calculations are highly desirable.

Finally we estimate the e-ph coupling constant for La$_2$C$_3$. Based on the Sommerfeld coefficient and the electronic structure calculation, we obtain $\lambda_{ph}$ from the determination of $\gamma_N$ using the equation $\gamma_N = (2\pi^2 k_B^2/3)N(E_F)(1+\lambda_{ph})$. From the DOS calculations for the 2% C deficient compounds, we take $N(E_F) = 1.75$ states/eV f.u. Using $\gamma_N = 10.6$ mJ/mol K$^2$, the estimated $\lambda_{ph}$ is 1.4 indicating that the La$_2$C$_3$ clearly belongs to the strong coupling regime.

In Fig. 11 we plot the calculated $T_c$ from the modified McMillan formula,

$$T_c = \frac{\omega_{in}}{1.2} \exp \left[ -\frac{-1.04(1 + \lambda_{ph})}{\lambda_{ph} - (1 + 0.62\lambda_{ph})\mu^*} \right],$$

with the measured $T_c = 13.4$ K (grey horizontal line). For comparison we also plot the calculated $T_c$ from the original McMillan formula. In both cases, the Coulomb pseudopotential $\mu^*$ is fixed to 0.1. With the original McMillan formula assuming the effective phonon frequency to be the same as the Debye frequency, we found that the measured $T_c$ is reproduced with weak e-ph coupling, $\lambda_{ph} \sim 0.75$. However such a weak coupling cannot reconcile with the results of specific heat and upper critical fields as discussed above. If we use the logarithmic averaged phonon frequency $\omega_{in}$ in the modified McMillan formula, Eq. (13), a large value of $\lambda_{ph}$ is necessary to reproduce the measured $T_c$. Because of the relatively large error for the calculated $T_c$ from the modified McMillan formula due to the reduced accuracy for determining $\omega_{in}$, it is difficult to determine the $\lambda_{ph}$ value precisely. However it is obvious that $\lambda_{ph}$ is larger than 1.3, which is in good agreement with the estimate from the comparison of the Sommerfeld coefficient.

![FIG. 11: The calculated $T_c$ from the modified McMillan formula (solid line) as a function of the e-ph coupling constant, $\lambda_{ph}$. The borders of the shaded (grey) areas represent the results obtained for the upper and lower bounds of $\omega_{in}$. For comparison, we also plot the calculated $T_c$ from the original McMillan formula with dashed line. The horizontal (dark grey) solid line denotes the measured $T_c$.](image-url)
In conclusion, specific heat and upper critical field studies were performed on the sesquicarbide superconductor La$_2$C$_3$ together with neutron powder diffraction as well as electronic structure calculations. The main conclusions are the followings. (i) The density of states near the $E_F$ is very sensitive to a small C deficiency in the sample, which provides an explanation for the wide scatter of $T_c$'s and superconducting properties observed in the previous reports. (ii) The temperature and magnetic field dependence of the specific heat is consistent with a single gap $s$-wave BCS superconductor. (iii) The logarithmic averaged phonon frequency for the superconductivity is quite low suggesting the importance of low energy phonon modes for the superconductivity. (iv) Even though the band splitting due to the non-centrosymmetry in the structure and the spin-orbit coupling is clearly confirmed by the electronic structure calculations, its effect seems not sizable enough to cause exotic superconducting properties as observed in other non-centrosymmetric superconductors. To conclude, all of the summarized features suggest that La$_2$C$_3$ is a strongly coupled BCS-type superconductor with an isotropic $s$-wave superconducting gap.

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The only difference of the original McMillan formular from Eq. (13) is that the coefficient $\omega_{\text{ln}}/1.2$ is replaced by $\Theta_{\text{D}}(0)/1.45$. See Ref. 63.