The rare earth sesquicarbides, $R_2C_3$, where $R$ is a rare earth or Y are a family of superconducting materials that form in the bcc $Pu_2C_3$ structure under high temperature conditions. Samples produced by arc melting have critical temperatures, $T_c$, of 10K to 12K, with little dependence on the particular rare earth. For example, as synthesized samples with the largest and smallest rare earths, specifically, La$_2C_3$ and Y$_2C_3$ have critical temperatures of 11K and 10.5K, respectively. However, it was found early on that heavy Th doping raises $T_c$ up to 17K in the case of the Y compound. Very recently, Amano and co-workers reported that $T_c$ for Y$_2C_3$ could be increased to 18K by synthesis under high pressure (4-5.5 GPa). The resulting samples have the same $Pu_2C_3$ structure as previously obtained samples but with a slightly different lattice parameter, suggesting that the effect of pressure is to change the composition of the samples. Furthermore, they reported that the results were sensitive to the sintering conditions. The lattice parameters varied in the range $a=8.181\text{Å}$ – $8.226\text{Å}$, with reported $T_c$ spanning the range 15K to 18K. The extrapolated upper critical field of the 18K samples was estimated to be $\approx 30T$.

The $Pu_2C_3$ structure has four formula units per primitive unit cell, spacegroup $I43d$, Y on site 16c ($u,u,u$) and C on site 24d ($v,0.1/4$), where the coordinates are in terms of the bcc lattice vectors (see Fig. 1). As may be seen, C dimers with short bond lengths are a characteristic of this structure. Electronic structure studies of other metals with C dimers both at the tight binding and density functional level suggest that the electronic structure could have substantial C-C antibonding character near the Fermi level. Such states may be expected to have extremely high deformation potentials, reflecting these very strong C-C triple bonds. Also reflecting the very strong covalent bonds, phonons that modulate the C-C distances would be very stiff, which, if these states were responsible for the superconductivity, would yield a moderate electron-phonon coupling, $\lambda$, and a very high logarithmic average phonon frequency and therefore high prefactor in the McMillan equation for $T_c$. In this scenario, a very strong dependence of $T_c$ on stoichiometry (more precisely, occupation of the antibonding states) might be anticipated, as well as the possibility of very high $T_c$ in more optimally doped samples, perhaps with values like in MgB$_2$ and Al$_3$C$_6$. Here we report density functional calculations of the electronic structure and the coupling constants of a C-C and an Y mode aimed at determining the extent to which this scenario applies in Y$_2C_3$.

The present calculations were done using the general potential linearized augmented planewave (LAPW) method, with local orbital extensions to relax linearization errors and to treat the semi-core states of Y, LAPW sphere radii of 2.0 $a_0$ and 1.24 $a_0$ were used for Y and C, respectively. Well converged basis sets (convergence tests were done) consisting of 4250 basis functions for the 20 atom primitive cell were used, along with converged Brillouin zone samplings. The core states were treated relativistically and valence states semirelativistically. For the crystal structure we used the reported bcc $I43d$ $Pu_2C_3$ structure with the experimentally determined lattice parameter, $a = 8.226\text{Å}$, from Ref. 7 but relaxed the internal coordinates using the calculated atomic forces. We found significant changes in the C-C dimer bond length from the available experimental refinement (Ref. 11). Specifically, we obtain a C-C distance of 1.33 Å, and a Y-C distance of 2.51 Å, corresponding to internal parameters, $u=0.0504$ and $v=0.2940$. The corresponding full symmetry Raman modes are an Y dominated mode at 175 cm$^{-1}$ and an almost pure C-C bond stretching mode at 1442 cm$^{-1}$. It seems likely that the difference between our results and the C position of Ref. 11 is related to difficulty in the refinement due to sample stoichiometry, which is an issue in these sesquicarbides, as mentioned above.

The calculated electronic band structure and corresponding electronic density of states (DOS) are given in Figs. 2 and 3, respectively. The Fermi surfaces are displayed in Fig. 5. The band structure agrees qualitatively...
with a very recent report by Shein and Ivanovskii, although there are noticeable differences in detail, presumably related to the different C-C bond length in that calculation.

The band structure shows a manifold of 12 C 2s derived bands extending from -14.9 eV to -6.2 eV, relative to the Fermi energy, $E_F$ (note that there are 12 C atoms in the primitive cell). This is followed by a narrower manifold of 18 C 2p bonding bands, associated with the C dimers. This, in turn, is separated by a $\sim 2.5$ eV gap from a broad manifold of mixed C-C antibonding and Y character. The Fermi level lies near 1 eV from the bottom of this manifold. Fig. 4 shows the contribution from states near $E_F$ to the charge density. The plot is for the energy range that contributes 1 e per unit cell going down from $E_F$. This electronic structure is consistent with a conventional picture of strongly covalently bonded C dimers embedded in a solid that has metallic cohesion involving mixture of Y and antibonding C states.

As may be seen, there are several bands crossing the $E_F$. This leads to a complex multisheet Fermi surface (Fig. 5), with no obvious strong nesting features. The density of states at $E_F$ is $N(E_F)=1.88$ eV$^{-1}$ on a per formula unit both spins basis, corresponding to a bare linear specific heat coefficient, $\gamma_{bare}=4.4$ mJ/mol K$^2$. This is approximately 60% larger than the experimental value of $\gamma = 2.8$ mJ/mol K$^2$ (ref. 2), but this comparison should be interpreted with caution since the experimental stoichiometry was not well established. We note that Th doped Y$_2$C$_3$ with $T_c=17$K (closer to the 18K reported for Y$_2$C$_3$ by Amano and co-workers), has a reported experimental $\gamma = 4.7$ mJ/mol K$^2$, and that the DOS is peaked at the stoichiometric composition, implying that off-stoichiometric samples would likely have lower $\gamma$, both because of lower $\gamma_{bare}$ and presumably lower electron phonon enhancement.

Considering the apparent absence of strong nesting, and the large unit cell (four formula units, 20 atoms), it is expected that the zone center modes may be at least semi-quantitatively representative for determining the electron-phonon coupling. As a further simplification, we focus on two modes in order to obtain the gross features. These are the two full symmetry zone center modes, it hardly seems reasonable for the bond stretching modes but underestimates the phonon frequency for the other modes, since the C dimers are lighter than an Y atom. However, considering the crudeness of representing the system with two full symmetry zone center modes, it hardly seems justified to attempt corrections, and instead we view the result as semi-quantitative.

The calculated electron-phonon coupling for the stoichiometric band filling is $\lambda = 0.6$ and is dominated by phonons other than the C-C bond stretching; the C-C bond stretching provides less than 10% of the total $\lambda$. Inserting $\lambda = 0.6$ into the McMillan formula, with $\mu^*=0.1$ and $\omega=175$ cm$^{-1}$, we obtain $T_c=5$K, which is fair agreement considering the crudeness of the approximation employed.

What is significant is that $\lambda$ has a maximum at the stoichiometric band filling. This is related to the fact that the Fermi energy falls on a peak in the DOS. The dependence of $\lambda$ on band filling and the difficult synthesis of stoichiometric sesquicarbides provides an explanation for the experimentally observed variability of $T_c$ depending on preparation conditions. Going to lower band filling, $\lambda$ decreases and then increases again to a value exceeding $\lambda = 1$, reflecting the structure of the DOS, but this only happens quite far down, corresponding to an electron deficiency of about 1 e per formula unit. The C-C stretching contribution is small throughout this region. Going to higher electron count, $\lambda$ again decreases initially and then increases, again to values exceeding $\lambda = 1$. However, in this case the C-C bond stretching contribution becomes significant and as a result the logarithmic average phonon frequency also sharply increases. In principle, this would mean that heavily electron doped Y$_2$C$_3$ would become a high temperature superconductor, like MgB$_2$ and A$_3$C$_60$. However, this is based on a rigid band filling, which is a highly unlikely scenario. Instead, population of C-C antibonding states should be highly disfavored, and therefore it would be rather difficult to chemically reach the region where this contribution to $\lambda$ becomes large.

In summary, we report electronic structure and mode electron-phonon calculations for Y$_2$C$_3$. The results are consistent with conventional electron-phonon mediated superconductivity related to Y - C phonons. The results show that the superconductivity is qualitatively like in other metal carbide superconductors, and not like MgB$_2$ or A$_3$C$_60$.

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![FIG. 1. Crystal structure of Y\textsubscript{2}C\textsubscript{3} showing the C\textsubscript{2} dimers. Large spheres denote Y and small spheres denote C.](image)

![FIG. 2. Calculated band structure of Y\textsubscript{2}C\textsubscript{3} with the relaxed atomic positions. The lowest bands shown are part of the C\textsubscript{2}s manifold. The bottom of this manifold is at -14.9 eV. The lower panel is a blow-up around $E_F$, which is at 0 eV.](image)

![FIG. 3. Electronic density of states of Y\textsubscript{2}C\textsubscript{3} with the relaxed atomic positions. The solid line is the total density of states on a per formula unit basis and the dashed line is the Y\textit{d} contribution as defined by projection onto the Y LAPW sphere of radius 2.0 $a_0$.](image)
FIG. 4. This figure shows the charge density originating from the valence bands near $E_F$ (see text) in 1/4 of the primitive unit cell around C (dumbbells, red online) and Y (interconnected network, blue online). Isodensity surfaces correspond to $\rho(r) = 0.00112 \, e/a_0^3$ for C and $0.00092 \, e/a_0^3$ for Y. Small differences between the charge density values were needed to improve visibility of the two surfaces. For the same purpose, the parts of the Y charge density surfaces, penetrating from the neighboring unit cells, were removed. Note the metallic like Y derived density and the C antibonding density.

FIG. 5. LDA Fermi surfaces of $Y_2C_3$.

FIG. 6. Mode $\lambda$ and average phonon frequency (see text) as a function of energy. The heavy dashed (heavy solid) line denotes the full symmetry Y (C) derived mode $\lambda$ as a function of energy, normalized as if these modes are representative. The light dashed line is the total $\lambda$ with this assumption. The light dotted line is the logarithmic average of these two frequencies with $\lambda$, which would enter the prefactor of the McMillan equation.