Electron-phonon superconductivity in noncentrosymmetric $LaNiC_2$: First-principles calculations

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We report first-principles calculations of the electronic structure and electron-phonon coupling in the noncentrosymmetric superconductor $LaNiC_2$. These show that the material is a conventional electron-phonon superconductor with intermediate coupling. There are large contributions to the coupling by two low-frequency C nonbond-stretching modes, one of which has strong Kohn anomalies. Since $LaNiC_2$ lacks inversion symmetry, the pairing is of dominant *s*-wave type with some mixture of *p*-wave character. This will give exponential decay in the specific heat.

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$LaNiC_2$ is a member of a family of ternary nickel carbides $RNiC_2$ (where R is a rare earth or Y) first reported by Bodak and Marusin.[1] These compounds form in the base centered orthorhombic $CeNiC_2$-type structure (space group $Amm2$) that lacks inversion symmetry. Studies of magnetic properties show that the $RNiC_2$ phases exhibit a variety of magnetic ordering for various R.[2,3] Although, Ni is often associated with magnetism, e.g., in oxides and in intermetallics, the magnetism in these compounds is due to $4f$ electrons of R with almost no magnetic contribution from Ni. Therefore, it is perhaps not surprising that $LaNiC_2$ does not show magnetic ordering. Interestingly, it is instead superconducting at $T_c=2.7$ K.[4,5]

Lee *et al.*[4] found nonexponential decay of specific heat below T_c and based on this argued that $LaNiC_2$ is an unconventional superconductor. Since pure Ni is a ferromagnet and Ni compounds are often magnetic, one might suppose $LaNiC_2$ to be near magnetism and therefore that a pairing mechanism involving spin fluctuations is operative. Spin fluctuations are not pairing for order parameters that do not change sign on the Fermi surface (i.e., conventional *s* wave). However, Pecharsky *et al.*[5] observed the usual exponential decay of specific heat below T_c, consistent with the conventional BCS superconductivity. One avenue to address the inconsistency of these two experiments is by determining the symmetry that is broken in the superconducting system. Gauge symmetry is broken in a conventional BCS superconductor[6] while other symmetries are broken in unconventional ones.[7] Related to this, Hillier *et al.*[8] recently reported their results of muon spin-relaxation measurements on $LaNiC_2$ that indicate that time-reversal symmetry is broken in the superconducting state. Such time-reversal symmetry breaking requires a superconducting state with triplet character and does not occur in singlet superconductors. However, this analysis is complicated by the noncentrosymmetric lattice structure of $LaNiC_2$.

There are a number of other examples of noncentrosymmetric superconductors including, for example, $CePtSi_3$, $CeIrSi_3$, $CeRhSi_3$, UIr, Li_2Pd_xB, Re_3W, and Y_2C_3.[9–15] These include both nonphonon-mediated heavy Fermion metals and electron-phonon superconductors, which behave very much like conventional centrosymmetric superconductors. Since parity is not a good quantum number in noncentrosymmetric systems, it necessitates modification of the scheme for classification of Cooper pairs. For example, Yanase and Sigrist[16] argue that Cooper pairs have a state that has dominant *p* wave with some mixture of *s*-wave symmetry in $CePt_3Si$. Considering the T_c of $LaNiC_2$, either case is possible; it could be a conventional electron-phonon superconductor in analogy with Y_2C_3 (Refs. 15 and 17) and Re_3W (Ref. 18) in which case it would have a Cooper pair state that has dominant *s* wave but some mixture of *p*-wave symmetry or alternatively it could be an unconventional superconductor in analogy with the noncentrosymmetric heavy Fermions such as $CePt_3Si$ (Refs. 9 and 19) or near ferromagnetic UIr, in which case it would have dominant *p* or *d* wave character, which would allow a simpler explanation of nonexponential behavior.

Here, we report the results of first-principles calculations of electronic structure, phonon dispersion, and electron-phonon coupling. We find that the main contributions to the electronic structure from Ni $3d$ orbitals are away from the Fermi energy and consequently that $LaNiC_2$ is nonmagnetic and rather far from magnetic instabilities that might lead to strong spin fluctuations thereby leading to an unconventional superconducting state. On the other hand, we obtain a value of electron-phonon coupling constant $\lambda \sim 0.52$ with logarithmically averaged frequency $\omega_{\ln} \sim 207$ cm^{-1}. Using simplified Allen-Dynes formula, we obtain $T_c \sim 3.0$ K that suggests $LaNiC_2$ is an intermediately coupled electron-phonon superconductor with dominant pairing that has *s* wave but also some mixture of *p*-wave symmetry.

$LaNiC_2$ forms in a base centered orthorhombic structure with La on site $(0.5,u,1-u)$, Ni on site (0,0,0), and C on site $(0,v,w)$. In this compound, the La atoms form trigonal prisms, which are alternately filled by Ni and C dimers, hence breaking the inversion symmetry. Another characteristic of this structure is the short bond length of C dimers, which indicates the existence of very stiff bond-stretching modes. If these modes were responsible for superconductivity, it would result in a moderately high electron-phonon coupling and a large logarithmically averaged phonon frequency.

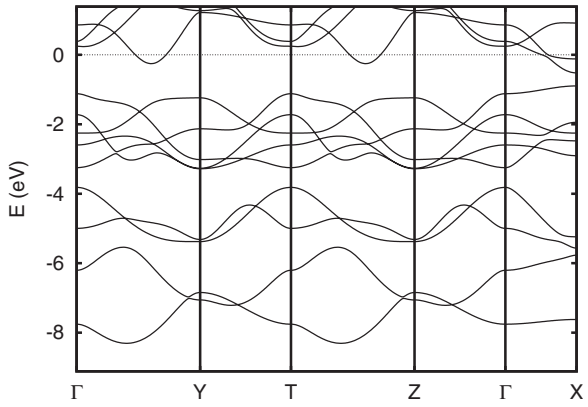

FIG. 1. Calculated LDA band structure of $LaNiC_2$ plotted along the path $(0,0,0)\rightarrow(0,\frac{1}{2},0)\rightarrow(0,\frac{1}{2},\frac{1}{2})\rightarrow(0,0,\frac{1}{2})\rightarrow(0,0,0)\rightarrow(\frac{1}{2},0,0)$.

This would mean a very high prefactor in the McMillan equation for T_c. Previous tight-binding[20] and density functional[17,21] studies of other metals with C dimers show that the electronic structure near the Fermi level could have substantial contributions from states with C-C antibonding character. If this were the case for $LaNiC_2$, there may be a strong dependence of T_c on the occupation of the antibonding states (which could be controlled by doping) and perhaps also a high T_c in optimally doped samples.

Our electronic-structure calculations were performed within the local-density approximation (LDA) using the general potential linearized augmented plane-wave (LAPW) method as implemented in our in-house code.[22] We used LAPW spheres of radius $2.0a_0$ for La and Ni and $1.25a_0$ for C. We repeated some calculations with the WIEN2K code[23] as a test and found no significant differences. We used the experimentally reported lattice parameters ($a=3.959$ Å, $b=4.564$ Å, $c=6.204$ Å) (Ref. 1) but relaxed the internal coordinates. We obtain for internal parameters, $u=0.3886$, $v=0.5411$, and $w=0.1606$. This yields the calculated C-C distance of 1.36 Å, which is in reasonable accord with the reported experimental value[1] of 1.41 Å.

The phonon dispersions and electron-phonon coupling were calculated using linear response as implemented in QUANTUM ESPRESSO code.[24] The linear-response calculations were also done using experimental lattice parameters, using ultrasoft pseudopotentials within the generalized gradient approximation (GGA) of Perdew *et al.*[25] An $8\times8\times8$ grid was used for the zone integration in the phonon calculations while a more dense $32\times32\times32$ grid was used for the zone integration in the electron-phonon coupling calculations. The basis set cutoff for the wave functions was 40 Ry while a 400 Ry cutoff was used for the charge density. The internal coordinates were again relaxed and we obtained values that agreed well with the values obtained from LDA calculations. The GGA and LDA electronic structures were very similar.

The calculated band structure and Fermi surface of $LaNiC_2$ is shown in Figs. 1 and 2, respectively. These agree in large scale features with recent calculations done by Laverock *et al.*[26] but the details of the Fermi surface and band dispersions differ significantly along some directions, yielding differences in the Fermi surface. These presumably reflect the use of nonfull potential methods in Ref. 26. The corresponding density of states is shown in Fig. 3. The band structure shows a C $2s$ derived band between -15.5 and -13.5 eV and another C $2s$ derived band between -8.5 and -6.5 eV, relative to the Fermi energy E_F. This is followed by a manifold of three bands with C $2p$ character, associated with C dimers that extend from -7.5 to -3.8 eV. This is followed by a manifold of five bands of Ni $3d$ character between -3.5 and -0.9 eV. These account for the majority of the Ni d character in the density of states although there is some Ni d contribution near E_F, similar to the borocarbides (e.g., $LuNi_2B_2C$), which electron-phonon superconductors.[27] There are two bands that cross the Fermi level and they have mixed Ni $3d$, La $5d$, and C $2p$ antibonding characters. This electronic structure is consistent with strongly bonded C dimers embedded in a metallic solid with states near E_F having La, Ni, and C antibonding character.

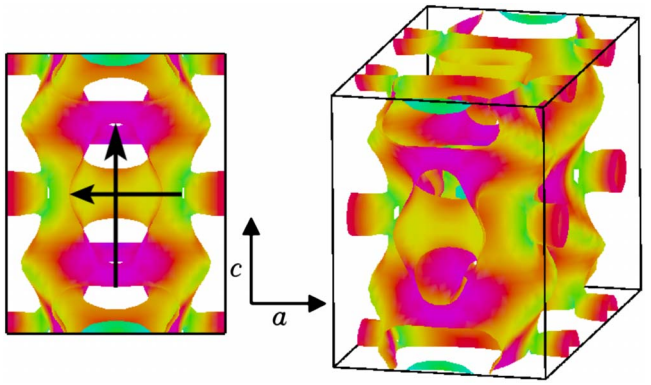

FIG. 2. (Color online) Calculated LDA Fermi surface of $LaNiC_2$. The shading is by velocity. The arrows indicate nesting vectors that give rise to Kohn anomalies.

The density of states at E_F is $N(E_F)=2.6$ eV^{-1} on a per formula unit, both spin basis. The calculated Fermi velocities are $\langle v_{xx}^2\rangle^{1/2}=1.79\times10^5$ m/s, $\langle v_{yy}^2\rangle^{1/2}=1.52\times10^5$ m/s, and $\langle v_{zz}^2\rangle^{1/2}=1.48\times10^5$ m/s, indicating only modest resistivity anisotropy unless there is a large scattering anisotropy. The density of states has a prominent peak with a maximum very close to E_F. Therefore the stoichiometric compound is ex-

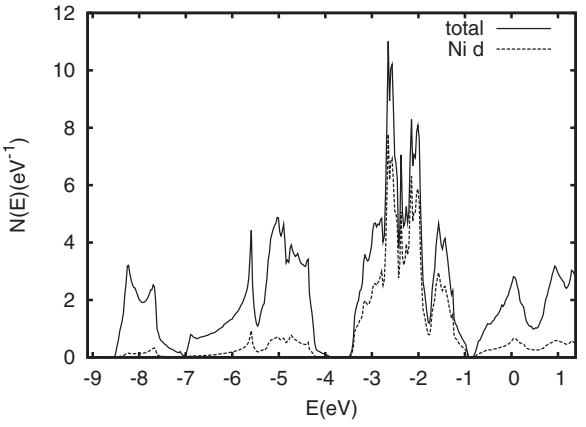

FIG. 3. Calculated LDA density of states of $LaNiC_2$ on a per formula unit both spins basis. The projection is onto the Ni LAPW sphere.

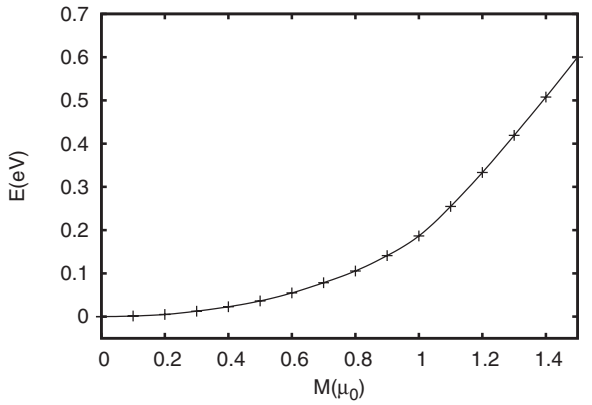

FIG. 4. Fixed spin moment magnetic energies for $LaNiC_2$.

pected to have the highest T_c similar to Y_2C_3, although in the present case the peak is broader. Doping away from stoichiometry will move the E_F away from the peak and is therefore expected to lower the T_c. The moderately high value of $N(E_F)$ might also indicate magnetism if the states at the Fermi level are of predominantly Ni d character. However, as mentioned, most of the Ni d states are in a manifold of five bands that lie between −3.5 and −0.9 eV relative to the Fermi level. Hence, the high $N(E_F)$ of $LaNiC_2$ does not place it near magnetism. This is supported by our fixed spin moment calculations. Figure 4 shows energies calculated for different values of magnetic moment relative to the nonmagnetic case. As may be seen the energy scale is relatively high, which means that the material is not near ferromagnetism.

The calculated phonon dispersions of $LaNiC_2$ are shown in Fig. 5. The corresponding phonon density of states and Eliashberg spectral function $\alpha^2F(\omega)$ are shown in Fig. 6. The phonon dispersions show a set of 11 bands extending up to ~530 cm^{-1}, separated by a gap of ~775 cm^{-1} from one high-frequency band that lies between 1305 and 1355 cm^{-1}. The bands below 180 cm^{-1} show contributions from La, Ni, and C while the bands between 180 and 255 cm^{-1} are derived mainly from motions of Ni and C atoms. Above 255 cm^{-1} the bands are dominated by motions of C atoms. The highest frequency band is an almost pure C-C bond-stretching mode, confirming the picture of strongly bonded C dimer inferred from band structure.

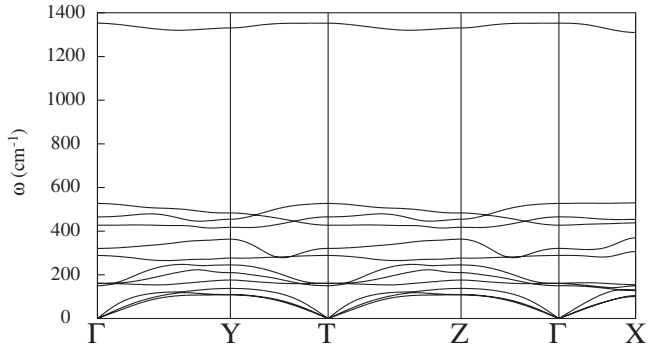

FIG. 5. Calculated phonon-dispersion curves of $LaNiC_2$ plotted along the path $(0,0,0)\rightarrow(0,\frac{1}{2},0)\rightarrow(0,\frac{1}{2},\frac{1}{2})\rightarrow(0,0,\frac{1}{2})\rightarrow(0,0,0)\rightarrow(\frac{1}{2},0,0)$.

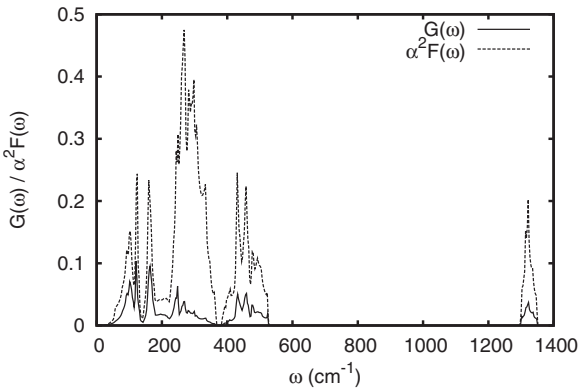

FIG. 6. Calculated phonon density of states and electron-phonon spectral function $\alpha^2F(\omega)$ for $LaNiC_2$.

The eighth branch of the phonon dispersion, which has mainly C nonbond-stretching character, shows Kohn anomalies at $k\sim(0,0.5,0.25)$, $k\sim(0,0,0.25)$, and $k\sim(0.25,0,0)$. These can be seen in Fig. 5 along the Y-T, Z-Γ, and Γ-X lines. The origin of the Kohn anomalies can be seen in the Fermi surface, which shows nesting with wave vectors $k\sim(0,0,0.25)$ and $k\sim(0.25,0,0)$ as indicated by two arrows in Fig. 2. A comparison of phonon density of states with the with the Eliashberg spectral function shows that the latter is enhanced relative to the former between 220 and 400 cm^{-1}, which is the region where the seventh (which also has mainly C nonbond-stretching character) and eighth branches are placed. We obtain a value of the electron-phonon coupling $\lambda_{ep}=0.52$. As there are 12 phonon branches, the average electron-phonon coupling per branch is $\lambda_{avg}=0.04$. The contribution due to seventh and eighth bands is large with values of $\lambda_7=0.13$ and $\lambda_8=0.09$, respectively. We obtain for the logarithmically averaged frequency $\omega_{\ln}=207$ cm^{-1}. Inserting these numbers into the simplified Allen-Dynes formula,

$$k_BT_c=\frac{\hbar\omega_{\ln}}{1.2}\exp\left\{-\frac{1.04(1+\lambda_{ep})}{\lambda_{ep}-\mu^*(1+0.62\lambda_{ep})}\right\} \quad (1)$$

with $\mu^*=0.12$, we obtain $T_c\sim3$ K, which is in accord with the experimental value of $T_c=2.7$ K.[4,5] While this close agreement may be partly fortuitous (note the parameter μ^* in the Allen-Dynes formula; 0.12 is a typical value but values in the range 0.1–0.15 are reasonable), it does indicate that the superconductivity can be readily explained in an electron-phonon framework.

To summarize, we report full potential calculations of the electronic structure, phonon dispersions of $LaNiC_2$, and electron-phonon coupling in $LaNiC_2$. We find that the conventional electron-phonon coupling picture readily describes the superconductivity of $LaNiC_2$. With inversion center this would yield a pure s-wave state. However, because of the noncentrosymmetric structure of $LaNiC_2$ a small p admixture will be present. The Ni d states are located mainly away from the Fermi energy and accordingly we do not find $LaNiC_2$ to be near magnetism. Therefore, we expect the contribution of spin fluctuations to the coupling, which is pair

breaking for *s* wave, to be small. The phonon-mediated Cooper pairs are intermediately coupled with large contributions made by two low-frequency C nonbond-stretching modes, one of which has Kohn anomalies. Owing to the lack of inversion symmetry, the pairing will have dominant *s*-wave character with some mixture of *p* wave. This is expected to give exponential decay of specific heat below T_C. In particular, there will be no line nodes in the gap function. Also, while the Cooper pairs also have some *p*-wave character, a pure electron-phonon mechanism will not yield breaking of time-reversal symmetry due to the removal of centrosymmetry.

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