Electron-phonon superconductivity in non-centrosymmetric LaNiC$_2$: first principles calculations

Alaska Subedi

Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996, USA and
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA

David J. Singh

Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114, USA

We report first principles calculations of the electronic structure and electron-phonon coupling in the non-centrosymmetric 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 non-bond-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.

PACS numbers: 74.70.Dd,74.25.Jb,74.25.Kc

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. These compounds form in the base centered orthorhombic CeNiC$_2$-type structure (space group $Ammm$) that lacks inversion symmetry. Studies of magnetic properties show that the $RNiC_2$ phases exhibit a variety of magnetic ordering for various $R$. Although, Ni is often associated with magnetism, e.g. in oxides and in intermetallics, the magnetism in these compounds is due to 4$f$ 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 $T_c = 2.7 \, K$.

Lee et al. found non-exponential 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. 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 while other symmetries are broken in unconventional ones. Related to this, Hillier et al. 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 non-centrosymmetric lattice structure of LaNiC$_2$.

There are a number of other examples of non-centrosymmetric superconductors including for example CePt$_3$Si, CeIrSi$_3$, CeRh$_2$Si, UiIr, Li$_2$Pd$_4$B, Re$_5$W and Y$_2$C$_3$. These include both non-phonon 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 non-centrosymmetric systems, it necessitates the modification of scheme for classification of Cooper pairs. For example, Yanase and Sigrist argue that Cooper pairs have a state that has dominant $p$-wave with some mixture of $s$-wave symmetry in CePt$_3$Si. Considering the $T_c$ of LaNiC$_2$, either case is possible; it could be a conventional electron-phonon superconductor in analogy with Y$_2$C$_3$ (refs. 15,17) and Re$_5$W (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 non-centrosymmetric heavy Fermions such as CePt$_3$Si (refs. 19,20), or near ferromagnetic UiIr, in which case it would have dominant $p$ or $d$ wave character, which would allow a simpler explanation of non-exponential 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 3$d$ orbitals are away from the Fermi energy and consequently that LaNiC$_2$ is non-magnetic 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 $\omega_0 \sim 207 \, cm^{-1}$. Using simplified Allen-Dynes formula, we obtain $T_c \sim 3.0 \, K$ that suggests LaNiC$_2$ is an intermediated 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 struc-
ture 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. This would mean a very high prefactor in the McMillan equation for \( T_c \). Previous tight-binding and density functional 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 planewave (LAPW) method as implemented in our in-house code.\(^{22}\) We used LAPW spheres of radius 2.0\( a_0 \) for La and Ni and 1.25\( a_0 \) for C. We repeated some calculations with the WIEN2k code\(^{26}\) as a test and found no significant differences. We used the experimentally reported lattice parameters \( a = 3.959 \text{ Å}, b = 4.564 \text{ Å}, c = 6.204 \text{ Å} \) 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 \( \text{Å} \), which is in reasonable accord with the reported experimental value of 1.41 \( \text{Å} \).

The phonon dispersions and electron-phonon coupling were calculated using linear response as implemented in QUANTUM ESPRESSO code.\(^{23}\) The linear response calculations were also done using experimental lattice parameters, using ultrasoft pseudopotentials within the generalized gradient approximation (GGA) of Perdew et al.\(^{24}\) An \( 8 \times 8 \times 8 \) grid was used for the zone integration in the phonon calculations, while a more dense \( 32 \times 32 \times 32 \) 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 agree 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.,\(^{20}\) 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 non-full 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 5 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\(_2\)B\(_2\)C), 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 character. 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.

The density of states at \( E_F \) is \( N(E_F) = 2.6 \text{ eV}^{-1} \) on a per formula unit both spin basis. The calculated Fermi velocities are \( < v_{xx}^2 >^{1/2} = 1.79 \times 10^5 \text{ m/s}, < v_{yy}^2 >^{1/2} = 1.52 \times 10^5 \text{ m/s}, \) and \( < v_{zz}^2 >^{1/2} = 1.48 \times 10^5 \text{ m/s}, \) 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-
expected to have the highest $T_c$ similar to Y$_2$C$_3$, 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 5 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. Fig. 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 electron-phonon spectral function $\alpha^2 F(\omega)$ are shown in Fig. 6. The phonon dispersions show a set of 11 bands extending up to $\sim$ 530 cm$^{-1}$, separated by a gap of $\sim$ 775 cm$^{-1}$ from 1 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, firming the picture of strongly bonded C dimer inferred from band structure.

The eighth branch of the phonon dispersion, which has mainly C non-bond-stretching character, shows Kohn anomalies at $k \sim (0, 0.5, 0.25)$ 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 wavevectors $k \sim (0, 0, 0.25)$ 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 non-bond-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 $\lambda_8 = 0.09$, re-
respectively. We obtain for the logarithmically averaged frequency \(\omega_n = 207 \text{ cm}^{-1}\). Inserting these numbers into the simplified Allen-Dynes formula,

\[
k_B T_c = \frac{\hbar \omega_n}{1.2} \exp \left\{- \frac{1.04(1 + \lambda_{ep})}{\lambda_{ep} - \mu^*(1 + 0.62\lambda_{ep})} \right\},
\]

with \(\mu^* = 0.12\), we obtain \(T_c \sim 3 \text{ K}\), which is in accord with the experimental value of \(T_c = 2.7 \text{ K}\).\(^{45}\) While this close agreement may be partly fortuitous (note the parameter \(\mu^*\) 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 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 non-centrosymmetric 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 intermediate coupled with large contributions made by two low frequency C non-bond-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.

We are grateful for helpful discussions with Lijun Zhang and support from the Department of Energy, Division of Materials Sciences and Engineering.

1. O.I. Bodak and E.P. Marusin, Dopov. Akad. Nauk. Ukr. RSR, Ser. A: Fiz.-Mat. Tekh. Nauki 41, 1048 (1979).
2. P. Kotsanidis and J.K. Yakinthos, Journal of the Less-Common Metals 152, 287 (1989).
3. H. Onodera, Y. Koshikawa, M. Kosaka, M. Ohashi, H. Yamauchi and Y. Yamaguchi, Journal of Magnetism and Magnetic Materials 182, 161 (1998).
4. W.H. Lee, H.K. Zeng, Y.D. Yao, and Y.Y. Chen, Physica C 266, 138 (1996).
5. V.K. Pecharsky, L.L. Miller, and K.A. Gschneidner, Phys. Rev. B 58, 497 (1998).
6. J. Bardeen, L.N. Cooper, and J.R. Schrieffer, Physical Review 108, 1175 (1957).
7. M. Sigrist and K. Ueda, Rev. Mod. Phys. 63, 239 (1991).
8. A.D. Hillier, J. Quintanilla, and R. Cywinski, Phys. Rev. Lett. 102, 117007 (2009).
9. E. Bauer, G. Hilscher, H. Michor, C. Paul, E.W. Scheidt, A. Gribanov, Y. Seropegin, H. Noel, M. Sigrist, and P. Rogl, Phys. Rev. Lett. 92, 027003 (2004).
10. N. Kimura, K. Ito, K. Saitoh, Y. Umeda, H. Aoki, and T. Terashima, Phys. Rev. Lett. 95, 247004 (2005).
11. I. Sugitani, Y. Okuda, H. Shishido, T. Yamada, A. Thamizhavel, E. Yamamoto, T.D. Matsuda, Y. Haga, T. Takeuchi, R. Settai, and Y. Onuki, J. Phys. Soc. Jpn. 75, 043703 (2006).
12. K. Togano, P. Badica, Y. Nakamori, S. Orimo, H. Takeya, and K. Hirata, Phys. Rev. Lett. 93, 247004 (2004).
13. T. Akazawa, H. Hidaka, T. Fujiwara, T.C. Kobayashi, E. Yamamoto, Y. Haga, R. Settai, and Y. Onuki, J. Phys. Condens. Matter 16, L29 (2004).
14. J.K. Hulm and R.D. Blaugher, J. Phys. Chem. Solids 19, 134 (1961).
15. G. Amano, S. Akutagawa, T. Muranaka, Y. Zenitani, and J. Akimitsu, J. Phys. Soc. Jpn. 73, 530 (2004).
16. Y. Yanase and M. Sigrist, J. Phys. Soc. Jpn. 76, 043712 (2007).
17. D.J. Singh and I.I. Mazin, Phys. Rev. B 70, 025004 (2004).
18. Y.L. Zuev, V.A. Kuznetsova, R. Prozorov, M.D. Vannette, M.V. Lobanov, D.K. Christen, and J.R. Thompson, Phys. Rev. B 76, 132508 (2007).
19. H. Mukuda, S. Nishide, A. Harada, K. Iwasaki, M. Yogi, M. Yashima, Y. Kitaoaka, M. Tsujino, T. Takeuchi, R. Settai, Y. Onuki, E. Bauer, K.M. Itoh, and E.E. Haller, J. Phys. Soc. Jpn. 78, 04705 (2009).
20. S. Lee, W. Jeitschko, and R.-D. Hoffmann, Inorg. Chem. 28, 4094 (1989).
21. Th. Guldén, R.W. Henn, O. Jepsen, R.K. Kremer, W. Schnelle, A. Simon, and C. Felser, Phys. Rev. B 56, 9021 (1997).
22. D.J. Singh and L. Nordström, Plane Waves, Pseudopotentials and the LAPW Method, 2nd Ed. (Springer, Berlin, 2006).
23. P. Blaha, K. Schwarz G.K.H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2K, An Augmented Plane Wave + Local Orbitals Program for for Calculating Crystal Properties (K. Schwarz, TU Wien, Austria, 2001), ISBN 3-9501031-1-2
24. P. Giannozzi et al., [http://www.quantum-espresso.org](http://www.quantum-espresso.org)
25. J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
26. J. Laverock, T.D. Haynes, C. Utfeld and S.B. Dugdale, arXiv:0903.1814
27. W.E. Pickett and D.J. Singh, Phys. Rev. Lett. 72, 3702 (1994).