Isotope Effect and Phonon Softening in Superconducting Borocarbides and Boronitrides

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Received 15.11.1995

Abstract

The isotope effect in the recently discovered class of superconductors LuNi$_2$B$_2$C and La$_3$Ni$_2$B$_2$N$_3$ is investigated in the context of electron-squeezed phonon interaction renormalizing the Ni-d electron-electron correlations. Squeezed phonon mode originates from the anharmonic character of the tetragonal Ni-B structure and is polarized in the vortical direction to the Ni layers. The isotope effect arises as a result of the zero point motion of the Ni-Ni d-electron hopping amplitude dominantly due to this vertical phonon mode. Within this model the isotope exponent is calculated to be $\alpha_B = 0.20$ as compared to the recently found experimental value $\alpha_{exp} = 0.27 \pm 0.10$. Finally, the phonon frequency softening predicted by our model electron-phonon interaction is discussed within the context of recent experiments on the relevant boron $A_{1g}$ softening.

74.20.Fg, 63.20.Ls, 71.27.+a, 74.70.Ad

Introduction

The superconductivity in $LnM_2B_2C$ where $Ln=\text{Y, Lu}$ and $M=\text{Ni, Pd}$, ...and $La_3Ni_2B_2N_3$ has shown that these quarternary compounds [1] form a new class of superconductors somewhere between the conventional and high $T_c$ ones [2]. It was suggested in the electron band theory calculations [2,3] that the superconductivity is due to a coupling of the boron $A_{1g}$ mode to the wide hybridized s-p electron band ($\sim 30eV$) in the Ni planes. According to the calculations carried out by various groups [3-5] there is a narrow (2-3 eV) density of states peak just below $E_F$ dominantly of Ni(3d) character. It was also
suggested [4-5] that relatively high $T_c$ is due to this large density of states; and, a shift in the peak position by additional 0.2 electrons/atom would put $E_F$ just on the peak, raising $T_c$ substantially. However in valence level photoemission measurements [6] of the normal state electronic structure of $YNi_2B_2C$ and in more recent photoemission and inverse-photoemission measurements [7] this peak in the density of states was not observed. Due to the slightly smaller Ni-Ni separation ($\sim 2.45\AA$) in the planes than in the pure Ni ($\sim 2.50\AA$) one expects strong electron-electron correlations in the Ni planes [4]. The observed bandwidth is 20-30% lower than the band theory calculations [2,3] likely due to the intratomic e-e correlations. Based on this reasoning, the normal basal resistivity of single crystals (LU,Y)(NiB)$_2$C is dominated by $T^2$ dependence at low temperatures [8]. Furthermore, superconductivity is not observed for Lu(M B)$_2$C with M=Co, Rh, Ir which all have less d-electrons than Ni. The latter implies the the crucial importance of the d-electron correlations for the occurrence of superconductivity. Also due to the light mass of the B atom, there is a strong electron-phonon coupling which is confirmed by the isotope effect measurements [9] and estimated by Pickett and Singth [4]. However, observation of the isotope effect by no means implies that phonon contribution to superconductivity is in the formation of pairs via an exchange mechanism [10]. The analysis of the temperature dependence of the magnetic susceptibility for the partially doped compound $YNi_{2-x}M_xB_2C$ where M=Co hints that the $T_c$ suppression is not due to the pairbreaking effects caused by the paramagnetic impurities [11,12]. On the other hand, in the cobalt doped compound $T_c$ is suppressed by a factor of two as compared to that of the copper doped compound M=Cu for the same doping $x \leq 0.2$. This fact cannot be accounted for within the BCS framework in terms of a slight reduction in the electron density of states in the case of cobalt substitution.

In this work we take the effect of boron lattice displacement into account in the hopping amplitude between $Ni(3d)$ electrons in the planes and suggest that the superconductivity is of kinematical origin [13] but is strongly renormalized by the high energy vertically polarized vibrations of the B atoms [4].

The small displacements in the strong Ni-B bonding in the in-plane Ni atomic equilibrium positions can be separated into the displacement in the layers and displacement perpendicular to the layers as [14],

$$r_{ij} = r_0 + u_{||} + \frac{1}{2r_0}u_{\perp}^2 + O(u^3),$$  \hspace{1cm} (1)

where $r_{ij}$ is the distance between the two neighbors in the Ni square planes; $r_0$ is the lattice constant ($r_0 \approx 2.45\AA$); and $u_{||}$ and $u_{\perp}$ are the displacements in the planar and the perpendicular directions respectively. The expansion of the Ni-Ni in-plane hopping integral with respect to small $u_{||}, u_{\perp}$ is then,

$$t_{ij}(r_{ij}) = t_{ij}^0 - \beta_{ij}\delta r_{ij},$$  \hspace{1cm} (2)

where $t_{ij}^0 = t_{ij}(r_0)$ is the bare hopping amplitude, and $\beta > 0$ is the absolute value of the first derivative of $t_{ij}^0$ with respect to the lattice constant and $\delta r_{ij} = r_{ij} - r_0$. Due to the
isotropy of Ni layers the linear in-plane displacement \( u_{ij} \) is negligible in comparison to \( u_{\perp} \).

The electron band is dominantly of Ni(3d) character. Considering the Ni-d orbital dynamics and their interaction with phonons separately, the Hamiltonian for this phonon-assisted interaction becomes [14],

\[
\mathcal{H} = \sum_{q, \lambda} \omega_{q, \lambda} \hat{b}_{q, \lambda}^\dagger \hat{b}_{q, \lambda} \\
+ \sum_{<i,j>, \sigma} \epsilon_{i, \sigma}^j c_{i, \sigma}^j \left\{ t^0 - \frac{\beta}{2r_0} \sum_{q', \lambda', \lambda} D^q_{q', \lambda'} (b_{q', \lambda'}^\dagger b_{q', \lambda'} + b_{q', \lambda'} b_{-q', \lambda'}^\dagger) \delta_{q, -q'} \delta_{\lambda', \lambda} \right\} \\
+ \mathcal{H}_{\text{intra}},
\]

where \( D^q_{q', \lambda'} = \frac{1}{2M_B N} \sqrt{\omega_{q', \lambda'} q' \lambda'} \). Here, the delta symbols indicate that the total phonon momentum is conserved independently from the electron momentum since \( q \) is orthogonal to the planes due to the longitudinal polarization with \( u_{\perp} \neq 0 \). All possible intraatomic interactions of different electron orbitals are included in the purely electronic last term. The operator \( b_{q, \lambda}^\dagger \) (\( b_{q, \lambda} \)) annihilates (creates) phonons with momentum \( q \) in the phonon branch \( \lambda \). The \( \omega_{q, \lambda} \) represents the phonon energy spectrum. We will now drop the branch index \( \lambda \) and assume that one (i.e. boron \( A_{1g} \)) vertical mode dominates [2]. \( M_B \) and \( N \) are the boron mass and the number of unit cells, respectively. The Hamiltonian (3) is of non-conventional an-harmonic electron-phonon coupling type because of its bilinear form with respect to \( u_{\perp} \) [15-17]. For the ground state of the Hamiltonian in (3) we analyze the form

\[
|\Psi_G \rangle = |\Psi_e \rangle \cdot |\Psi_{ph} \rangle
\]

with \( |\Psi_e \rangle \) describing the normal metallic state and with

\[
|\Psi_{ph} \rangle = \prod_q S(\xi_q)|0\rangle = \prod_q \exp \left\{ \xi_q (b_{q}^\dagger b_q^\dagger - b_q b_{-q}) \right\} |0\rangle
\]

describing the squeezed phonon vacuum state, where \( \xi_q \) is a variational parameter.

We represent by fig.1 curve (a) the shift in the hopping integral \( \delta t \) in Eqs. (2) and (3) as a function of the dimensionless squeezed coupling constant \( \eta/\omega_0^2 = \frac{\gamma}{2M_B \omega_0^2} \) with [14]

\[
\gamma = \frac{\beta}{2r_0} \sum_{<i,j>, \sigma} \epsilon_{i, \sigma}^j c_{i, \sigma}^j.
\]

Variation with respect to \( \xi_q \) yields [14] \( e^{-4\xi_q} = 1 - \frac{4\gamma D_q}{\omega_q^2} \) for the minimized ground state energy where \( D_q = D^q_{q, \lambda} \delta_{q, -q} \delta_{\lambda, \lambda'} \). Using this \( \xi_q \), in Figure 1 by curve (b) we present the shift \( \Delta E \) in the ground state energy \( E_G = \langle \Psi_G | \mathcal{H} | \Psi_G \rangle \) due to \( \xi_q \neq 0 \) from

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its value when $\xi = 0 (i.e., \Delta E = E_{G}^{\text{vac}} - E_{G}^{\text{sq}})$. It appears that in the range $0 \leq n \omega_{0}^{2} \leq 0.08$ the squeezed vacuum phonon ground state is energetically favorable.

The band structure of Ni-d electrons is composed of the completely filled $e_{g}$ and partially filled $t_{2g}$ levels (i.e. Ni(3$d^{7+2}$)). The upper correlated band (UCB) of $t_{2g}$ is formed due to the transitions from the polar quadruplets to the ground state triplets. The lower correlated band (LCB) is formed due to the itineracy of the intraatomic transitions between 3-particle triplet ground state and the 2-particle excited polar state.

All the symmetry properties of the electron basis functions are included in the irreducible representations of $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, $\frac{9}{2}$ and $\frac{11}{2}$ by cyclic permutation of their indices. Here $\alpha$ indicates the set of all possible transitions. In Ref. [14] it was calculated that $\langle \sum_{<i,j>, \sigma} c_{i} \sigma c_{j, \sigma} \rangle = f \sum_{\alpha} g_{\alpha}^{2}$ with $f = (9 - 2n)/36$ being the end factor consisting of populations of the ground state triplet and polar quadruplet levels. Using this result with Eq.’s (9) and (10) we find

$$\gamma = \frac{\beta f}{2x_{0}}[(\frac{1}{\sqrt{3}})^{2} + (\sqrt{\frac{2}{3}})^{2} + (1)^{2}]$$

(8)

Recently it was shown that it is possible to realize kinematical superconductivity [13] due to strong Ni-d electron-electron correlations with the critical temperature in the UCB given by [14],

$$T_{c} = \frac{W}{3} \sqrt{7n(1-n)} \exp \left\{ -\frac{\gamma^{6}}{16 - n} \right\}$$

(9)

Here $W = 2t$ is the Ni(3d) electron half bandwidth with $n$ describing the number of Ni-d electrons in the UCB of Ni$^{3+2/2}(3d^7-n)$ plane. From the charge balance we also have $n = l/m$ for the general class $(LnC)_{3}(NiB)_{m}$ [14,18]. Near the 3-particle ground state Ni$^{3+2/2}(3d^7-n)$ the superconductivity exists in Ni borocarbides and boronitrides at the bottom of the UCB ($0 < n < n_{\text{crit}}^{LCB} = 9/16$) and at the top of the LCB ($n_{\text{crit}}^{LCB} = 9/16 - n < 0$) as shown in the Fig.2. In accordance with the calculations of Ref. [19] we neglect the occupation number of carbon valence electron orbitals and assume hereon the effective charge $Q = -4$ in the superconducting compound Ln$^{3+3}(Ni^{3+2}B^{-3})_{2}C_{2}$. So in the Ni borocarbide the itinerant d-electron concentration corresponds to the theoretically superconducting region $n = -0.5 > n_{\text{crit}}^{LCB}$.

In this framework, the suppression of $T_{c}$ in $LnNi_{2-x}M_{x}B_{2}C_{2}$, where $M$=(Co, Cu, Fe, Ru), is based on the fact that Co(3$d^{7}$) possesses one less d-electron and, $Fe^{+2}(3d^{4}4s^{2})$ and $Ru^{+2}(4d^{5}5s)$ possess two less d-electrons compared to Ni. The effect of doping is to shift the point $n=-0.5$ (for pure nondoped Ni compound) to the left on the $T_{c}$ curve.
This explanation is true provided that doping does not change the structural properties of the lattice. Remarkably for Co the a-axis remains unchanged [20] up to x=0.6. The Cu substitution causes a sharp increase in the a parameter which in turn suppresses $T_c$. Here the weakening of the Ni-B bonds is also important in the context of this model since it weakens the squeezed coupling constant.

Using Eqs. (3), (4) and (5) the renormalized electron half bandwidth is found to be

$$W = 2t^0(1 - \frac{\beta}{2r_0\gamma^2} \sum_q \frac{\eta}{\omega_q (1 - \frac{1}{\omega_q})}).$$  (10)

Inspecting Eqs. (6) and (8), for realistic phonon density of states [14], two contributions can be seen to have dependence on the boron mass in Eq. (10). The first one comes directly from the momentum summation over the phonon spectrum and it scales with the characteristic phonon frequency $\omega_0$. This term plays the key role in the large value of the isotope exponent. The other contribution is by the mass dependence of $\gamma$. The isotope effect is calculated from $\alpha_B = -\partial nT_c/\partial nM_B$. Using Eqs. (7) and (8) we find,

$$\alpha_B \sim M_B \frac{\partial (\delta t/t^0)}{\partial M_B} = \frac{1}{2} \frac{\delta t}{t^0} + \frac{\omega_0}{t^0} \frac{\partial}{\partial \ln u} \left( \frac{\delta t}{\omega_0} \right), \quad u = \eta/\omega_0^2. \quad (11)$$

The approximation in Eq. (11) holds due to the adiabaticity condition $\omega_0/t^0 \sim 0.1 \ll 1$. The first term is the contribution of the phonon energy spectrum whereas the second one is that of the $\beta$ with $\nu = \partial n/\partial nM_B$. To estimate $\nu$ we consider the renormalized hopping amplitude in the standard form,

$$t \simeq t^0 e^{-k r},$$  (12)

where $k^{-1}$ is the radial extend of the Ni-d electron orbital and $r$ is given by Eq. (1). The ionic d-electron radii for $Ni^{2+}$ is about 0.8 Å and that for $Ni^{3+}$ is about 0.5Å. Since the average valency of Ni ions in superconducting samples is intermediate between +2 and +3, we roughly take $k^{-1} = 0.6-0.7Å$. From Eqs (1) and (12) with a typical $u_{\perp}/r_0 \simeq 0.1$ and $r_0 = 2.45Å$, we find $v \simeq 0.015$. The finite squeezing $\eta/\omega_0^2 \simeq 0.045$ produces a further 5-10% increase in the value of $u_{\perp}$. Nevertheless, the contribution of the second term in (11) is proportional to $v \delta t/t^0$ and can still be neglected. Using these, one finds from Eq. (11) $\delta t/t^0 \sim \delta u_{\perp}$, which yields a rough estimate of $\alpha_B \approx 0.2$. The change in $\beta$ with respect to $M_B$ is negligible but $\delta t/t^0$ in Eq. (11) is still relatively large as compared to other narrow band superconductors, and also being proportional to $\omega_0$, causes a large isotope effect. In [14] we have previously overestimated $\nu$ and underestimated $\delta t/t$. This incorrectly resulted in the second term yielding the dominant contribution in (11).

The value of $\beta$ can be inferred directly from the curve (b) of Fig.1. With $n = 0.5$ for the $LuNi_2B_2C$ compound and $\omega_0 \simeq 106meV$ corresponding to the boron $A_{1g}$ vibrations as estimated in Ref.[4], $\eta/\omega_0^2 \simeq 0.045$ yields $\beta \simeq 1.2eV/Å$. Then we find $t \simeq k^{-1} \beta \simeq 0.7eV$ and $\delta t \simeq \beta u_{\perp} \simeq 0.27 eV$. From here one obtains $\alpha_B \simeq 0.19$.
Very recently, the inelastic neutron scattering experiments on single crystal $\text{LuNi}_2\text{B}_2\text{C}$ have been performed [21] and the phonon dispersions have been measured. The c-polarized vibrations display anomalous temperature behaviour particularly in the vicinity of the zone boundary [1/2,0,0]. The phonon frequencies are observed to be strongly renormalized by softening effects for both acoustic and optical c-polarized vibrations as the temperature is lowered across $T_c$. In Ref. [21] the highest branch measured has a zone center frequency of 24meV which is far below the 106 meV optical c-polarized $A_{1g}$ mode predicted by Pickett and Singh [4]. As they also conclude there, the effect of the observed softening is not yet clear since no experimental data is available beyond 24 meV and hence, the comparison with the detailed electron-phonon interaction models is still lacking.

Comparing Eqs. (3) and (4) as well as Ref.[15], the renormalized phonon frequency is given by,

$$
\Omega_{q,\lambda} = \sqrt{\tilde{\omega}_{q,\lambda}^2 - 4|\kappa_{q,\lambda}|^2}
$$

(13)

where in our case,

$$
\tilde{\omega}_{q,\lambda} = \omega_{q,\lambda} - 2\gamma D_{q,\lambda}^{-q,\lambda}, \quad \kappa_{q,\lambda} = \frac{1}{2}\tilde{\omega}_{q,\lambda} \tan \frac{\hbar \xi_{q,\lambda}}{4}
$$

(14)

and at zero temperature $\gamma$ and $\xi_{q,\lambda}$ are as given above by minimizing the ground state energy. We notice that $\Omega_{q,\lambda}$ has a similar trend to the anomalies observed in Ref.[21] as the temperature is lowered below $T_c$ so it is an interesting quantity to examine with respect to $T$. Since, from the experimental data, $T_c/\omega_0 \sim 10^{-2}$ we safely assume that the two phonon coherence imposed by the ground state in (5) is not destroyed to a large extend for temperatures below $T_c$. Therefore, the thermal behaviour for $T \leq T_c$ is dominated by the excitations of the correlated phonons above the ground state given by Eq. (5). In this temperature range the shift in the phonon frequencies can be attributed to the changes in the temperature dependent ground state parameter $\xi_q$ which depends on the thermal electron occupation number through the relation below Eq. (6). We calculate the temperature dependence of $\xi_q$ using Eq.'s (6), (13) and (14) from,

$$
\Delta \omega_{q,\lambda} = \Omega_{q,\lambda} - \omega_{q,\lambda} \simeq -2(\gamma D_{q,\lambda}^{-q,\lambda} + |\kappa_{q,\lambda}|^2/\omega_{q,\lambda})
$$

(15)

both contributions in the bracket are positive and increase with decreasing temperature; hence $\Delta \omega_q < 0$. The first term contains $\gamma$ which has a regular dependence on the temperature via the thermal occupation factors as well as the temperature dependent gap. The temperature dependence of in the bracket via $\gamma$ and $\kappa_{q,\lambda}$ is defined in Eq. (6) and (14). In Fig.(3.a) below, the temperature dependence of the phonon dispersion across $T_c$ is shown. The zero temperature limit of our calculations is normalized consistently with respect to $\gamma D_q \simeq \eta/\omega_0^2=0.045$ as suggested by the ground state calculation in Fig.(1). The softening starts at $T_c$ and increases monotonously as the temperature is lowered below $T_c$. The corresponding numerical solution $\xi_q$ as a function of temperature is shown in Fig. (3.b). The exact momentum dependence of the phonon softening is determined
by the details of the model dependence of $\beta$ on the phonon wave vector. The important fact is that, at low temperatures the softening in this optical mode can be as large as $35\%$ which is within the observed experimental range [21].

Figure 1. (a) The renormalization $-\delta t/\omega_0$ of the electron hopping amplitude. (b) Shift in the ground state energy $(E_G^{\text{vac}} - E_G^{\text{sq}})\omega_0$. Here the superscripts denote the zero temperature ground state energy calculated in the vacuum state $|0\rangle$ and in the squeezed vacuum state $S(\xi)|0\rangle$, respectively.

Figure 2. The normalized superconducting transition temperature $T_c/W$ as a function of electron concentration $n$ in the upper and lower correlated bands.

Figure 3. (a) The softened phonon frequency $\Omega_q/\omega_q$ as a function of temperature $T/W$. For doping level $n=0.25$ the maximal obtainable critical temperature is $T_c \simeq 0.2W$ from Fig. (2). (b) Temperature dependence of the phonon ground state correlation parameter $\xi_q$. 
Similar models of electronic bandwidth renormalization have been proposed [22] for the isotope effect observed in alkali-metal-doped $C_{60}$. It is known that phonon dynamics can implicitly appear in the electronic degrees of freedom yielding strong isotope effect without requiring any phonon-exchange mechanism [10]. Compatible ideas were also suggested to explain the observation of the isotope effect in the oxide superconductors [23] and in superconducting fullerenes [22,24].

In summary, we have attempted a possible explanation of the isotope effect in the superconducting Ni based borocarbides and boronitrides using the electron-squeezed phonon interaction. We have shown that squeezed phonon naturally arises as a result of the absence of the linear Fröhlich electron-phonon coupling in the perpendicular direction to the metallic Ni layers. Our earlier [14] and present calculations indicate that the superconductivity is of kinematical origin [13] and the electron-electron correlations are renormalized by their interaction with squeezed phonons which in turn leads to a substantial isotope effect. The calculated numerical value of $\alpha_B$, however, is very prone to large uncertainties due to the inherent sensitivity of it on the material dependent estimates of $\kappa$ and $u_J$. One aspect of our electron-phonon interaction model is that a softening of the phonon frequency is expected starting at $T_c$ and increasing as the temperature is further lowered below $T_c$ which is also observed experimentally for the $A_{1g}$ symmetric $z$ polarized boron vibrations [21]. It is not very easy to measure the dynamical changes in the properties of the phonon ground state wavefunction. However, the frequency softening, enhancement in the zero point amplitudes and other non-perturbative effects are signatures of ground state anomalies. In particular, another way to experimentally confirm frequency softening for the relevant boron modes is to look for anomalies in the low temperature zero-point fluctuations in the amplitude of boron displacement $<u_z^2>^{1/2}$ in the $z$-direction. The observed large values [21] of the low temperature phonon frequency softening of the order of $\% 35$ can produce temperature dependent amplitudes as large as twice the harmonic zero point fluctuations. These large temperature dependent effects are observable by measuring the atomic Debye-Waller factor using inelastic neutron scattering and EXAFS techniques which recently started to become valuable tools for the lattice dynamics. A number of such experiments have revealed a rich dynamical structure of temperature dependent phonon anomalies in most high temperature superconductors [25].

Acknowledgments

T.H. is thankful to Professor N.M. Plakida for a fruitful discussion. V.I. acknowledges discussions with Professors Y. Murayama and H. Inokuchi. Both authors thank the referee for taking their attention to Ref.[21].

References


[12] Here we do not discuss the magnetic borocarbides where the 4f magnetism competes with the superconductivity (e.g. Gd$_{1-x}$Y$_x$Ni$_2$B$_2$C, Y$_{1-x}$Er$_x$Ni$_2$B$_2$C, Y$_{1-x}$AxNi$_2$B$_2$C (A=Sm, Dy.)


[16] Similar non-linear electron couplings have been recently studied also for the LBCO and YBCO type high temperature superconductors [see Jinsuk Song and James F. Annett, Phys. Rev., B 51 (1995) 3840; Granse, J. Haertwich, J. Schreiber et. al. in Proceedings of the International Seminar on High Temperature Superconductivity, 28 June-1 July 1989, Dubna Russia, Eds. V.L. Aksenov, N.N. Bogolubov and N.M. Plakida (World Scientific 1989)]. The non-linearity of the perpendicular component is a direct consequence of the tetragonal symmetry which is also shared to a good extend by most of the copper-oxide superconductors.
[17] In the strong coupling Nambu-Eliashberg formalism the second order electron-phonon interaction was studied in: V.Z. Kresin, H. Morawitz and S.A. Wolf, *Mechanisms of Conventional and High-Tc Superconductivity* (Oxford Univ. Press 1993) where it was shown that the anharmonic contribution in the phonon self-energy raises $T_c$.

[18] There are not many experimental data about boronitrides. Assuming in superconducting $LN_3(3-3n)B_3$ the realistic magnitude $\delta = 0.3$ (see the last one of Ref.[1]) and effective charge $= -3$ we get $n=9/20$ from charge balance which is less than the predicted critical $n_{crit}=9/16$ in Eq.(9) for the existence of superconductivity.


[22] N.W. Ashcroft and M. Cyrot, Europhys. Lett., 23 (1993) 605. (One must note that in fullerenes the electronic mean free path is extremely short due to inherent imperfections. Here our analogy is not based on comparing the mechanisms of superconductivity in these two systems but rather on the renormalization of electronic degrees of freedom in both due to electron-phonon interaction.)

