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Isotope Effect and Phonon Softening in Superconducting Borocarbides and Boronitrides

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Abstract

The isotope effect in the recently disvovered class o superconductors $LuNi_2B_2C$ and $La_3Ni_2B_2N_3$ is investigated in the context of electron-squezed 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 $\alpha_B \leq 0.20$ as compared to the recently found experimental value α_B^{exp}=0.27∓0.10. Finally, the phonon frequency softening predicted by our model eletron-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=Y, Lu and M=Ni, Pd, ...and $La_3Ni_2B_2N_2$ 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 ($\sim 2.45\mathring{A}$) in the planes than in the pure Ni ($\sim 2.50\mathring{A}$) 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 intraatomic 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 Ln(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 occurence 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 dependene of the magnetic susceptibility for the partially doped compound $YNi_{2-x}M_xB_2C$ where M=Co hints that the T_c supression 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],

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

where r_{ij} is the distance between the two neighbors in the Ni square planes; r_0 is the lattice constant ($r_0 \simeq 2.45\mathring{A}$); 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,

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

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 $u_{||}$ 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],

$$\begin{aligned}\mathcal{H} &= \sum_{q,\lambda} \omega_{q,\lambda} b^{\dagger}_{q,\lambda} b_{q,\lambda} \\ &+ \sum_{<i,j>,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} \left\{ t^0 - \frac{\beta}{2r_0} \sum_{q,q',\lambda,\lambda'} D^{q',\lambda'}_{q,\lambda} (b^{\dagger}_{q,\lambda} + b_{-q,\lambda})(b^{\dagger}_{q',\lambda'} + b_{-q',\lambda'}) \delta_{q,-q'} \delta_{\lambda,\lambda'} \right\} \quad (3) \\ &+ \mathcal{H}_{intra},\end{aligned}$$

where $D^{q',\lambda'}_{q,\lambda} = \frac{1}{2M_B N \sqrt{\omega_{q,\lambda} \omega_{q',\lambda'}}}$. 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 $b_{q,\lambda}, (b^{\dagger}_{q,\lambda})$ annihilates (creates) phonons with momentum q in the phonon branch λ. The $\omega_{q,\lambda}$ represents the phonon energy spectrum. We will now drop the branch index λ 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

$$|\Psi_G> = |\Psi_e> . |\Psi_{ph}> \quad (4)$$

with $|\Psi_e>$ describing the normal metallic state and with

$$|\Psi_{ph}> = \prod_q S(\xi_q)|0> = \prod_q exp\left\{ \xi_q (b^{\dagger}_{-q} b^{\dagger}_q - b_{-q} b_q) \right\} |0> \quad (5)$$

describing the squeezed phonon vacuum state, where $\in_q$ is a variational parameter.

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

$$\gamma = \frac{\beta}{2r_0} \langle \sum_{<i,j>,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} \rangle. \quad (6)$$

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

its value when $\xi_q = 0(i.e., \Delta E = E_G^{vac} - E_G^{sq})$. It appears that in the range $0 \leq \eta\omega_0^2 \leq 0.08$ the squeezed vacuum phonon ground state is energetically favorable.

The band structure of Ni-d electrons is composed of the completely filled e_q and partially filled t_{2g} levels (i.e. Ni$(3d^{7+n})$=$Ni(e_g^4 t_{2g}^{3-n})$. The upper correlated band (UCB) of t_{2g} is formed due to the transitons 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 representation of t_{2g} as $a_\sigma = (xy), b_\sigma = (yz), c_\sigma = (zx)$. The expansion of the electron annihilation operator with respect to these basis functions can be made in terms of the possible intraaatomic transitions through the Hubbard-Okubo X operators as [14],

$$a_\sigma = \sum_\alpha g_\alpha X_\alpha = \frac{\sigma}{\sqrt{3}} X_{T_{\bar{\sigma}}} + \sqrt{\frac{2}{3}} \sigma X_{T_{\bar{\sigma}}}^{2aT_{bc}} + \sigma X_{\bar{\sigma}\bar{\sigma}\bar{\sigma}}^{2\bar{\sigma}\bar{\sigma}} + \cdots \tag{7}$$

and simlarly for b_σ and c_σ by cyclic permutation of their indices. Here α indicates the set of all possible transitions. In Ref. [14] it was calculated that $< \sum_{<i,j>,\sigma} c_i, \sigma^\dagger c_{j,\sigma} >= f \sum_\alpha g_\alpha^2$ 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

$$\gamma = \frac{\beta f}{2r_0}[(\frac{1}{\sqrt{3}})^2 + (\sqrt{\frac{2}{3}})^2 + (1)^2]. \tag{8}$$

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

$$T_c = \frac{W}{3}\sqrt{7n(1-n)} \exp\left\{ -\frac{(\frac{3}{4})^6}{\frac{9}{16} - n} \right\} \tag{9}$$

Here $W = 2t$ is the Ni(3d) electron half bandwidth with n describing the number of Ni-d electrons in the UCB of $Ni^{+3/+2}(3d^{7-n})$ plane. From the charge balance we also have $n = l/m$ for the general class $(LnC)_l(NiB)_m$ [14,18]. Near the 3-particle ground state $Ni^{3-n}(3d^{7+n})$ the superconductivity exists in Ni borocarbides and boronitrides at the bottom of the UCB ($0 < n < n_{crit}^{UCB} = 9/16$) and at the top of the LCB ($n_{crit}^{LCB} = -9/16 < n < 0$) as shown in the Fig.2. In accordance with the calculations of Ref. [19] we can neglect the occupation number of carbon valence electron orbitals and assume hereon the effective charge Q=-4 in the superconducting compound $Ln^{+3}(Ni^{3-n}B^{-3})_2C^Q$. So in the Ni borocarbide the itinerant d-electron concentration corresponds to the theoretically superconducting region $n = -0.5 > n_{crit}^{LCB}$.

In this framework, the suppression of T_c in $LnNi_{2-x}M_xB_2C$;, where M=(Co, Cu, Fe, Ru), is based on the fact that $Co(3d^7 4s^2)$ possesses one less d-electron and, $Fe^{+2}(3d^6 4s^2)$ and $Ru^{+2}(4d^6 5s)$ 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 supresses 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

$$W = 2t^{\circ}(1 - \frac{\beta}{2r_0\gamma t^0}\sum_q \frac{\eta}{\omega_q}\frac{1}{(1-\frac{4\eta}{\omega_q^2})}). \tag{10}$$

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 ω_0. This term plays the key role in the large value of the isotope exponent. The other contribution is by the mass dependence of β. The isotope effect is calculated from $\alpha_B = -\partial lnT_c/\partial lnM_B$. Using Eqs. (7) and (8) we find,

$$\alpha_B \sim M_B\frac{\partial(\delta t/t^0)}{\partial M_B} = \frac{1}{2}\frac{\delta t}{t^0} + \nu\frac{\omega_0}{t^0}\frac{\partial}{\partial lnu}(\frac{\delta t}{\omega_0}), \qquad u = \eta/\omega_0^2. \tag{11}$$

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 β with $\nu = \partial ln\beta/\partial lnM_B$. To estimate ν we consider the renormalized hopping amplitude in the standard form,

$$t \simeq t^0 e^{-kr}, \tag{12}$$

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 \simeq$0.6-0.7Å. From Eqs (1) and (12) with a typical $u_\perp/r_o \simeq 0.1$ and $r_0 = 2.45\mathring{A}$, 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 $\nu\delta t/t^0$ and can still be neglected. Using these, one finds from Eq. (11) $|\delta t|/t^0 \sim \kappa u_\perp \leq 0.4$ which yields a rough estimate of $\alpha_B \leq 0.2$. The change in β 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 ω_0, causes a large isotope effect. In [14] we have previously overestimated ν and underestimated $\delta t/t$. This incorrectly resulted in the second term yielding the dominant contribution in (11).

The value of β 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 $\beta \simeq 1.2$eV/Å. Then we find $t \simeq \kappa^{-1}\beta \simeq 0.7eV$ 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 $LuNi_2B_2C$ 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,

$$\Omega_{q,\lambda} = \sqrt{\tilde{\omega}^2_{q,\lambda} - 4|\kappa_{q,\lambda}|^2} \tag{13}$$

where in our case,

$$\tilde{\omega}_{q,\lambda} = \omega_{q,\lambda} - 2\gamma D^{-q,\lambda}_{q,\lambda}, \qquad \kappa_{q,\lambda} = \frac{1}{2}\omega_{q,\lambda} \tan h 4\xi_{q,\lambda} \tag{14}$$

and at zero temperature γ 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 chnages in the temperature dependent ground state parameter ξ_q which depends on the thermal electron occupation number through the relation below Eq. (6). We calculate the temperature dependence of ξ_q using Eq.'s (6), (13) and (14) from,

$$\Delta\omega_{q,\lambda} = \Omega_{q,\lambda} - \omega_{q,\lambda} \simeq -2(\gamma D^{-q,\lambda}_{q,\lambda} + |\kappa_{q,\lambda}|^2/\omega_{q,\lambda}) \tag{15}$$

both contributions in the bracket are positive and increase with decreasing temperature; hence $\Delta\omega_q < 0$. The first term contains γ 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 γ 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 ξ_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 β 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].

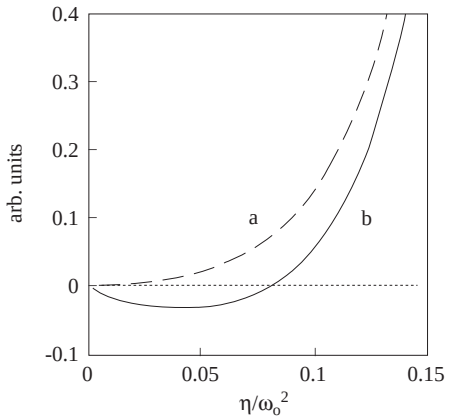

Figure 1. (a) The renormalization $-\delta t/\omega_0$ of the electron hopping amplitude. (b) Shift in the ground state energy $(E_G^{vac} - E_G^{sq})\omega_0$. Here the superscripts denote the zero temperature ground state energy calculated in the vacuum state $—0\rangle$ and in the squeezed vacuum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

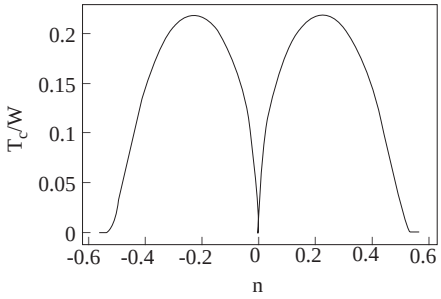

Figure 2. The normalized superconducting transition temperature T_c/W as a function of teh electron concentration n in the upper and lower correlated bands.

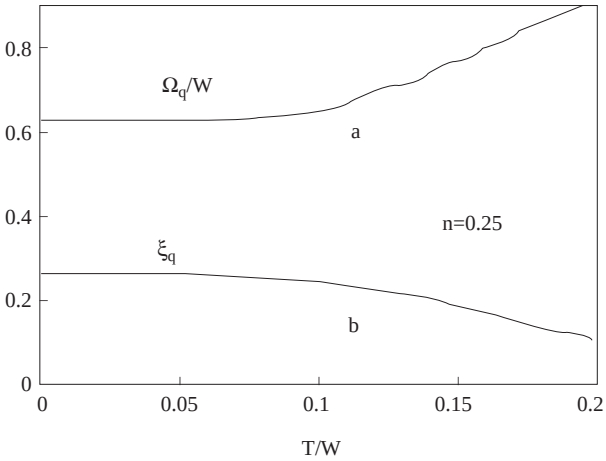

Figure 3. (a) The softened phonon frequency Ω_q/ω_q as a function of temperature T/W. For doping level n=0.25 the maximal obtainable critical temperature is $T_c \simeq 0.2W$ from Fig.(2). (b) Temperature dependence of the phonon ground state correlation parameter ξ_q.

Similar models of electronic bandwith 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 phonos which in turn leads to a substantial isotope effect. The calculated numerical value of α_B, however, is very prone to large uncertainties due to the inherent sensitivity of it on the material dependent estimates of κ and $u_\perp$. 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 $< u_\perp^2 >^{1/2}$ 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

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References

[1] C. Mazumdar, R. Nagarajan, G. Godart et al., Sol. St. Comm., **87** (1993) 413; R. Nagarajan et al., Phys. Rev. Lett., **72 N3** (1994) 274; R.J. Cava, H. Takagi, B. Batlogg et al., Nature,

367 (1994) 146; R.J. Cava, H. Takagi, H.W. Zandbergen et al., **367** (1994) 252; T. Siegrist, H.W. Zandbergen, R.J. Cava et al., Nature, **367** (1994) 254; R.J. Cava, H.W. Zandbergen, B. Batlogg et al., Nature, **372** (1994) 245.

[2] L.F. Mattheiss, T. Siegrist and R.J. Cava, Sol. St. Comm., **91** (1994) 587.

[3] L. Mattheiss, Phys. Rev, **B 49** (1994) 13279.

[4] W.E. Pickett and D.J. Singh, Phys. Rev. Lett, **72** (1994) 3702.

[5] R. Coehoorn, Physica, **C228** (1994) 331.

[6] M.S. Golden, M. Knupfer, M. Kielwein et al., Europhys. Lett. **28** (1994) 369.

[7] A. Fujimori, K. Kobayashi, T. Mizokawa et al., Phys. Rev., **B 50** (1994) 9660.

[8] H. Takagi, R.J. Cava, H. Eisaki et al.., Preprint (1994).

[9] D.D. Lawrie and J.P. Franck, Physica **C 235-240** *Proceedings of* $M^2S - HTSC - IV$ Grenoble, France, Ed. P. Wyder (Elsevier 1994).

[10] W. Buchel and B. Stritzker, Phys. Lett., **A 43** (1973) 403.

[11] H. Schmidt, M. Muller and H.F. Braun, Preprint (1994).

[12] Here we do not discuss the magnetic borocarbides where the 4f magnetism competes with the superconductivity (e.g. $Gd_xY_{1-x}Ni_2B_2C, Y_{1-x}Er_xNi_2B_2C, Y_{1-x}A_xNi_2B_2C$ (A=Sm,Dy.)

[13] V.A. Ivanov, Physica, **C162** (1989) 1485; V.A. Ivanov and R.O. Zaitsev, In. J. Mod. Phys., **B3** (1989) 1403; I.S. Sandalov and M. Richter, Phys. Rev. **B50** (1994) 12855; Y. Murayama and S. Nakajima, J.Phys.Soc.Jpn. 61(1991) 4265; Y. Murayama and S. Nakajima, J. Supercond. **7** (1994) 909.

[14] T. Hakioğlu, V.A. Ivanov, A.S. Shumovsky and B. Tanatar, *Phonon Squeezing in the Superconductivity of borocarbides* Physica-**C 235-240** (1994) 2343 *Proceedings of* $M^2S-HTSC-IV$, Grenoble France, Ed. P. Wyder (Elsevier December-1994); T. Hakioğlu, V.A. Ivanov, A.S. Shumovsky and B. Tanatar, Physica, **C 234** (1994) 167.

[15] T. Hakioğlu, V.A. Ivanov, A.S. Shumovsky and B. Tanatar, Phys. Rev., **B 51**, (1995) 15363.

[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-T_c 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 $LN_3(Ni^{(3-n)}B^3)_2N^{3-\delta}$ 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 critial n_{crit}=9/16 in Eq.(9) for the existence of superconductivity.

[19] R. Coehorn, Physica, **C 228** (1994) 331.

[20] A.K. Gangopadhyay, A.J. Schuetz, J.S. Schilling, Physica **C 246** (1995) 317.

[21] P. Dervenagas, M. Bullock, J. Zarestky et al., Phys. Rev, **B 52,** (1995) R9839.

[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.)

[23] D.S. Fisher, A.J. Millis, B. Shraiman et al., Phys. Rev. Lett., **61** (1987) 482.

[24] S. Chaktavarty, S.A. Kivelson, M.I. Salkola et al., Science, **256** (1992) 1306.

[25] B.H. Toby, T. Egami, J.D. Jorgensen et al. Phys. Rev. Lett., **64** (1990) 2414, M. Arai, K. Yamada, Y. Hidaka et al. Phys. Rev. Lett.,**69,** (1992) 359.