Phonon squeezing in superconducting borocarbides

T. Hakioğlu, V.A. Ivanov *, A.S. Shumovsky, B. Tanatar

Physics Department, Bilkent University, Bilkent, TR-06533, Ankara, Turkey

Abstract

The recently discovered superconductor $LuNi_2B_2C$ is investigated in the context of strong electron–electron correlations modulated by a squeezed phonon mode propagating in the perpendicular direction to the layers with longitudinal polarization. The squeezed phonons arise in the anharmonic lattice expansion since the linear electron–phonon interaction vanishes due to the structure of the NiB_4 tetrahedra. The observed weak isotope effect and small dependence of T_c on pressure is qualitatively understood within the framework of this model.

The observation of a superconducting phase transition in the intermetalic compound $LuNi_2B_2C$ has been reported in a number of recent publications [1–5]. There is strong evidence to believe that these Ni based boride carbides are the first example of a new family of superconductors [6]. Recently calculated electronic band properties [6,7] suggest that the almost filled Ni d electron band (2–3 eV) has a peak in the density of states slightly centered below E_F. On the other hand in the crucial valence level photoemission measurement of the normal-state electronic structure of YNi_2B_2C [8] the peak [6,7] was not observed in the Ni electron density of states because of the effects of strong electron–electron correlations. However, it was suggested that the interaction of the high-frequency boron optical a_{1g} mode with the unusually broad s–p band (30 eV) might play some role in the superconductivity of borocarbides. The a_{1g} zone-center optical modes correspond to the vertical displacement of boron atoms with respect to the Ni planes. It should be noted that the presence of the transition metal is the key to the important role of the electron–electron correlations in the formation of the superconducting state. On the other hand, the layered crystalline structure of this new type shows the possible contribution of transverse phonons as also implied by the boron isotope effect measurements [9]. In fact several band features with respect to their position around the E_F are found to be extremely sensitive to the NiB_4 tetragonal geometry. Therefore, in the present publication we would like to note the main peculiarities of electron–phonon coupling in borocarbides of the general class $(LnC)_l(NiB)_m$.

The crystal structure [5] consists of the square-planar Ni layers sandwiched between the B planes. The boron atoms form the tetrahedra together with the nickel atoms and Ni–B shear is sandwiched between the Lu–C planes. The a_{1g} phonons contribute via deformations of the tetragonal NiB_4 bond angles and in the planes they modulate the hopping amplitude through second-order effects. Due to the strong Ni–B coupling small shifts in the Ni atomic equilibrium positions can be separated into displacement in the layers and displacement perpendicular to the lay-

* Corresponding author. Address: Institute for Molecular Science, Okazaki National Research Institutes Center, Myodaiji, Okazaki 444, Japan.

ers. Then it follows from a simple geometric consideration that [10]

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

where r_{ij} is the distance between two neighbors in the Ni square planes, r_0 is the lattice constant ($r_0 \simeq 2.45$ Å [5]), $u_\parallel$ and $u_\perp$ are the displacements in the plane and in the perpendicular directions, respectively. The expansion of the hopping integral with respect to small $u_\parallel$ and $u_\perp$ is,

$$t_{ij}(r_{ij}) = t_{ij}^0 - \beta_{ij} \left(u_\parallel + \frac{1}{2r_0} u_\perp^2 \right) , \qquad (2)$$

where $t_{ij}^0 = t_{ij}(r_0)$ and $\beta > 0$ is the absolute value of the first derivative of t_{ij} with respect to the lattice constant. Because of the isotropy in the Ni layer the linear term in Eq. (2) is negligible in comparison with the bilinear term in $u_\perp$. Therefore the phonon contribution in the lowest order is represented by the square of the displacement in the transverse direction to the Ni layers. This type of higher-order electron–phonon interaction can lead to an effective electron–electron interaction produced by the phonon exchange. In transition-metal superconductors the influence of the e–e interactions on the electron–phonon interaction and visa versa is more important than that in conventional metals with high screening [11,12]. There the lattice vibrations lead to the variations of tunneling amplitude t and site energies ϵ [13] as

$$\delta t = t - t^0 = -\frac{t}{r_0} u_{ij} ,$$

$$\delta \epsilon = \epsilon - \epsilon^0 = -\gamma U \left(\frac{u_{ij}}{r_0} \right)^2 , \qquad (3)$$

where u_{ij} describes the relative displacement of ions between neighboring sites i, j and $\gamma \sim 1$. Considering that $u_\perp / r_0 \sim 0.1$, our electron–phonon contribution to the site energies $\delta \epsilon_i \sim 10^{-2} U \simeq 0.1$ eV for Coulomb interaction $U \sim 10$ eV (according to Ref. [8] the lower threshold value is about $U \sim 5$ eV) and $\delta t \sim 0.1 t$ is essential in calculating the ground-state properties. For non-degenerate electrons of one kind the hamiltonian of this phonon-assisted interaction can be written as

$$\mathcal{H} = \sum_{q,\lambda} \omega_{q,\lambda} b_{q,\lambda}^\dagger b_{q,\lambda}$$

$$+ \sum_{\langle i,j \rangle, \nu, \sigma} n_{i,\sigma}^\nu \left\{ \epsilon^0 - \frac{U}{r_0^2} \sum_{q,q',\lambda,\lambda'} D_{q,\lambda}^{q',\lambda'} (b_{q,\lambda}^\dagger + b_{-q,\lambda}) \right.$$

$$\times (b_{q',\lambda'}^\dagger + b_{-q',\lambda'}) \delta_{q,-q'} \delta_{\lambda,\lambda'} \bigg\}$$

$$+ \sum_{\langle i,j \rangle, \nu, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} \left\{ t^0 - \frac{\beta}{2r_0} \sum_{q,q',\lambda,\lambda'} D_{q,\lambda}^{q',\lambda'} (b_{q,\lambda}^\dagger + b_{-q,\lambda}) \right.$$

$$\times (b_{q',\lambda'}^\dagger + b_{-q',\lambda'}) \delta_{q,-q'} \delta_{\lambda,\lambda'} \bigg\} + \mathcal{H}_{\text{intra}} . \qquad (4)$$

Here the delta symbols indicate the total phonon-momentum conservation independently from the electron momentum since q is orthogonal to the planes. All possible intra-atomic interactions of electrons in different orbitals ν are included in the last term. The operator $b_{q,\lambda}$ ($b_{q,\lambda}^\dagger$) annihilates (create) phonons with momentum q in the phonon branch indicated by λ. The $\omega_{q,\lambda}$ represents the phonon energy. The $n_{i,\sigma}^\nu = c_{i,\sigma}^{\nu\dagger} c_{i,\sigma}^\nu$ is the number operator of electrons in the ν orbital with spin projection σ at site i of the Ni plane. In Eq. (4) we have

$$D_{q,\lambda}^{q',\lambda'} = \frac{1}{2MN \sqrt{\omega_{q,\lambda} \omega_{q',\lambda'}}} , \qquad (5)$$

where N is the number of unit cells and M is the reduced mass of the nickel and boron atoms. The ground-state eigenfunction can be chosen in the simplest form of a direct product of electron and phonon wave functions

$$|\psi_G \rangle = |\psi_e \rangle |\psi_{ph} \rangle . \qquad (6)$$

It is known in the context of narrow band polaron modes that the hamiltonian (4) supports the formation of the squeezed vacuum ground state in the form

$$|\psi_G \rangle = \prod_q \mathcal{S}(\xi_q) |0 \rangle$$

$$= \prod_q \exp\{ \xi_q (b_{-q}^\dagger b_q^\dagger - b_{-q} b_q) \} |0 \rangle , \qquad (7)$$

with ξ_q being the variational squeezing parameter. This new squeezed phonon state has first been applied to condensed matter physics in the intermediate valence problem [14,15], bipolaron superconductivity [16] and the superconductivity in the

Hubbard model [17]. In Refs. [16] and [17] the variational procedure was applied to calculate the superconducting state induced by the e–ph interaction. In our model due to the nature of the e–ph interaction the electron momentum is not coupled to the phonon momentum. This indicates that the phonons are not of conventional exchange type, therefore the ground state of the electrons is not of BCS but of metallic type. We will study the superconductivity in our suggested borocarbide model caused by the interaction of d electrons. In conventional superconductors due to the large coherence length only properties averaged over a large number of unit cells are important. In new superconductors, however, the coherence length is typically defined by few (~ 10–30) unit cells and the complexity of different branches in the phonon spectrum with different ion masses is very high. Here we consider the simplest and natural starting point and assume only the phonon branches transverse to the Ni planes with an averaged dispersion given by

$$\frac{1}{\omega^2} = \sum_\lambda \frac{1}{\omega_\lambda^2}.$$ (8)

In our one-parameter variational ground state, the ground-state energy E_g is calculated by minimizing

$$E_g = \langle \psi_e | \langle \psi_{ph} | \mathcal{H} | \psi_{ph} \rangle | \psi_e \rangle$$ (9)

with respect to the squeezing parameter ξ_q. With the help of the relation

$$\mathcal{S}^\dagger(\xi_q) b_q \mathcal{S}(\xi_q) = c_q b_q + s_q b_{-q}^\dagger,$$ (10)

where $c_q = \cosh 2\xi_q$ and $s_q = \sinh 2\xi_q$, we first calculate the effective hamiltonian with one orbital electrons (dropping the index ν),

$$\mathcal{H}_e = \langle \psi_{ph} | \mathcal{H} | \psi_{ph} \rangle$$

$$= \sum_{\langle ij \rangle, \sigma} n_{i,\sigma} \left\{ \epsilon^0 - \frac{U}{r_0^2} \sum_q D_q (c_q + s_q)^2 \right\}$$

$$+ \sum_{i,\sigma} c_{i\sigma}^\dagger c_{j\sigma} \left\{ t^0 - \frac{\beta}{2r_0} \sum_q D_q (c_q + s_q)^2 \right\}$$

$$+ \sum_q \omega_q s_q^2 + \mathcal{H}_{intra}.$$ (11)

Then using Eqs. (9) and (11), E_g is found to be minimum for $e^{-4\xi_q} = \{ 1 - 4\kappa D_q / \omega_q \}^{1/2}$ and

$$\kappa = \frac{\beta}{2r_0} \left\langle \sum_{\langle ij \rangle, \sigma} c_{i,\sigma}^\dagger c_{j,\sigma} \right\rangle + \frac{U}{r_0^2} \left\langle \sum_{i,\sigma} n_{i,\sigma} \right\rangle.$$ (12)

The expectation values in Eq. (12) are taken in the metallic ground state. The renormalization of the hopping amplitude t_{ij}^0 and the site energy ϵ_i^0 are finally found as

$$\delta t = -\frac{\beta}{2r_0 \kappa} \sum_q \frac{\eta}{\omega_q} \frac{1}{\left(1 - \frac{4\eta}{\omega_q^2} \right)},$$

$$\delta \epsilon = -\frac{U}{r_0^2 \kappa} \sum_q \frac{\eta}{\omega_q} \frac{1}{\left(1 - \frac{4\eta}{\omega_q^2} \right)},$$ (13)

where $\eta / \omega_q = (\kappa / 2MN\omega_q)$ describes the energy scale for the anharmonic e–ph coupling. In the calculation of Eqs. (13) we consider the phonon density of states $\rho(\omega)$ as a one-peak broadened function which smoothly vanishes for $\omega \leq 2\sqrt{\eta}$ and for $\omega \geq \omega_0$. In Fig. 1(a) the first of Eqs. (13) (δt as a function of η / ω_D^2) is given. Fig. 1(b) is the shift in the ground state energy ΔE_g described by the full electron–phonon part of the hamiltonian (11) with squeezed coupling from that without, as a function of the squeezed coupling η / ω_D^2. It can be seen that for $0 \leq \eta / \omega_D^2 \leq 0.08$ the
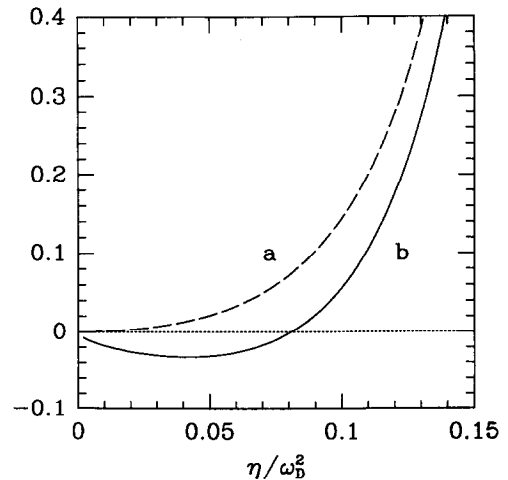

Fig. 1. (a) Renormalization of the hopping amplitude δt as a function of the squeezed coupling constant η / ω_D^2; (b) The shift in the ground-state energy ΔE_g of the electron–phonon part of the hamiltonian (11) with squeezed coupling from that without a function of the squeezed coupling constant η / ω_D^2.

squeezed phonon ground state is energetically favoured. The minimum of E_g in Fig. 1 corresponds to $\eta/\omega_D^2 \sim 0.04$–$0.05$.

Because of the partially filled d shell of the Ni ion embedded in the compound $(LnC)_l(NiB)_m$, strong d–d correlations are expected to be important in the planes. In the layered superconducting compound $La_{2-x}Sr_xNiO_4$ the octahedral oxygen surrounding leads to splitting of the electron energy in the completely filled lower t_{2g} levels and partially filled upper e_g levels where diamagnetic anomalies are observed [18,19]. In borocarbides tetrahedral boron surrounding [5] leads to completely filled lower e_g levels and partially filled upper t_{2g} levels with electron wave function of different angular symmetry xy, yz, xz. Therefore the effective electron hamiltonian of our problem is more complicated than Eq. (11). Because of the ideal boron surrounding in borocarbides, let us assume three-fold orbital degeneracy of Ni electrons participating in the superconductivity (contrary to the two-fold e_g degeneracy in nickelates [20]). The basis functions of electrons will be classified corresponding to the irreducible representation of t_{2g}: $a = (xy)$, $b = (yz)$, $c = (zx)$. Let us take for the vacuum state the half filled shell t_{2g}^3 of ion $M(d7) = M(e_g^4 t_{2g}^3) = Ni^{3+}$, Pd^{3+}, ... Then the quartet ground state can be expressed as (four triplets)

$$|\sigma\sigma\sigma\rangle = a_\sigma^\dagger b_\sigma^\dagger c_\sigma^\dagger |0\rangle, \qquad S_z = 3\sigma/2, \sigma = \pm 1,$$

$$|T_\sigma\rangle = \frac{1}{\sqrt{3}}(a_{\bar\sigma}^\dagger b_\sigma^\dagger c_\sigma^\dagger + a_\sigma^\dagger b_{\bar\sigma}^\dagger c_\sigma^\dagger + a_\sigma^\dagger b_\sigma^\dagger c_{\bar\sigma}^\dagger)|0\rangle,$$

$$S_z = \sigma/2. \tag{14}$$

In the tight-binding method of correlated electrons [21,22] the general intraatomic hamiltonian can be diagonalized in terms of triplets (14), "quadruplets" $(2--)$, $(2++)$, $(2_a T_{bc})$ where $2_a = \sigma a_\sigma^\dagger a_{\bar\sigma}^\dagger |0\rangle$ is the Hubbard "doublet" of the a orbital and $T_{bc} = \frac{1}{2}\sqrt{2}(b_\sigma^\dagger c_{\bar\sigma}^\dagger + b_{\bar\sigma}^\dagger c_\sigma^\dagger)$ is a triplet state with $S_z = 0$ "doublets" etc. The corresponding eigenenergy levels ϵ_p of $\mathscr{H}_{intra}$ include all essential intraatomic interactions (Hubbard, Coulomb, Hund). In terms of these eigenenergies we have $\mathscr{H}_{intra} = \sum_p \epsilon_p X_p^p$ the generalized Hubbard–Okubo X operators [23] $X_s^p = X_\gamma(p, s)$ project the energy state p into s differing by one electron configuration. The correlated energy bands are formed due to the itinerary character of the intraatomic transitions.

In the electronic structure of borocarbides the upper correlated band of t_{2g} electrons (involving the eighth d electron of $Ni^{3+/2+}$ ion) is formed due to the transitions from polar "quadruplets" to ground state "triplets". The expansion of the one-electron annihilation operator in terms of the orthogonal X operators is determined by the genealogical coefficients g_γ [23]

$$a_\sigma = \sum_\gamma g_\gamma X_\gamma(p, s)$$

$$= \frac{\sigma}{\sqrt{3}} X_{T_\sigma}^{2\sigma\sigma} + \sqrt{2/3}\sigma X_{T_\sigma}^{2aT_{bc}} + \sigma X_{\sigma\sigma}^{2\bar\sigma\bar\sigma} + ... \tag{15}$$

and similarly for b_σ and c_σ by cyclic permutation of the indices. In the presence of strong intraatomic d–d correlations the effective hamiltonian describing the normal phase of borocarbides is

$$\mathscr{H} = \sum_{\gamma, \langle i,j \rangle, a} g_\gamma^a g_\gamma^a X_i^\gamma X_j^\gamma - \mu \sum_i n_i \tag{16}$$

where t_{aa}^0 is given by Eq. (13) and μ is the chemical potential which includes the effect of narrowing of the energy bands due to phonon squeezing. Because of the angular symmetry of the basis functions $\psi_{xy,xz,yz}$ the interorbital hopping vanishes (i.e. $t_{ab}^0 = t_{ac}^0 = t_{bc}^0 = 0$).

Here the lifetime effects due to retardation and spin flip processes [24,25] are ignored. Due to the strong intraatomic correlations $(U \gg t)$ we may also confine intraatomic transitions defined in Eq. (15) forming the upper correlated band of t_{2g} electrons with single-particle energies,

$$\xi_p = f \sum_\gamma g_\gamma^2 t_p - \mu = f(\tfrac{1}{3} + \tfrac{2}{3} + 1)t_p - \mu, \tag{17}$$

where $t_p = \sum_\delta t^0 e^{p \cdot \delta} = 2t^0(\cos p_x r_0 + \cos p_y r_0)$ and $f = n_3 + n_4$ is the end factor [23] of the generalized DT, consisting of populations of the ground-state "triplet" levels n_3 and polar "quadruplet" levels n_4. Taking into account the four-fold and six-fold degeneracy of "triplets" and "quadruplets" in the expansion of Eq. (15) we obtain

$$4n_3 + 6n_4 = 1,$$

$$4n_3 + 3n_4 = \frac{3-n}{3}, \tag{18}$$

where n is the number of electrons in the upper correlated band of $Ni^{3+/2+}$ (d^{7+n}) plane. Therefore as-

suming in the compound $(Ln^{3+}C^{2-})_l(Ni^{3-n}B^{3-})_m$ the same distribution of charge as in Ref. [10], the charge balance requires $n=l/m$ and

$$f = n_3 + n_4 = \frac{9+2n}{36} . \qquad (19)$$

The equation for the chemical potential follows from

$$n = 3 + 2f \sum_\gamma g_\gamma^2 T \sum_{p,\omega_M} G_\gamma(p, \omega_M) e^{i\omega_M \delta}$$

$$= 3 + \frac{3+2n}{9} \sum_p \theta(-\xi_p) , \qquad (20)$$

where ω_M are the Matsubara frequencies. For rectangular density of states $\rho(\omega) = (1/2W)(\theta(W^2 - \epsilon^2)$ we get from Eq. (19)

$$\frac{\mu}{W} = \frac{9-16n}{18} , \qquad (21)$$

where the half band width $W=2t$ and t is given by Eqs. (3) and (13). Eqs. (17), (19) and (21) determine the one-particle energies ξ_p, forming the upper correlated band in the normal state. With decreasing temperature, the superconducting transition is found from the self-consistent solution of the homogeneous Bethe-Salpeter vertex as the (kinematical superconductivity [23,24])

$$1 = \sum_p \frac{t_p}{\xi_p} \tanh \frac{\xi_p}{2T_c} . \qquad (22)$$

In the logarithmic approximation the solution is described by

$$T_c = \frac{W}{3} \sqrt{7n(1-n)} \exp\left\{-\frac{(\frac{3}{4})^4}{\frac{9}{16}-n}\right\} \qquad (23)$$

The superconductivity exists for $n=l/m<\frac{9}{16}$ (i.e. superconducting compound with chemical formula LuCNi$_2$(3d^7)B$_2$). In agreement with the baric measurements we get an only dT_c/dp in agreement with the experiment [2]. The unusual isotope effect [9] can also be explained by the boron mass dependence of the prefactor in Eq. (23).

The renormalized half band width W can be computed from Eqs. (12) and (13). The boron isotope effect can be found from the mass dependence of the dimensionless parameter η/ω_D^2. In Fig. (1(a)) δt is shown as a function of the dimensionless ratio $u=\eta/\omega_D^2$. Due to the large band width, we have $\omega_D/t^0 \ll 1$.
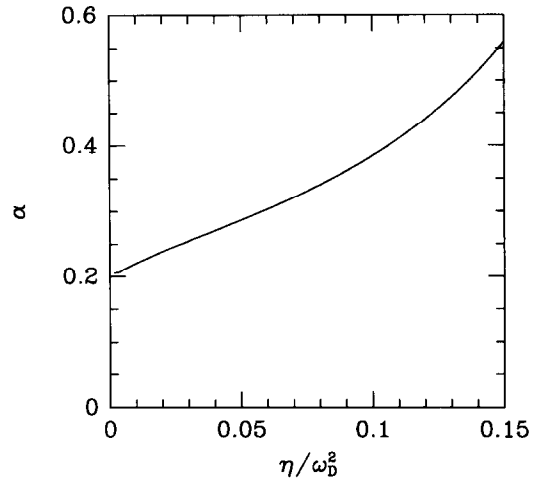

Fig. 2. The boron isotope exponent α_B as a function of the squeezed coupling constant η/ω_D^2.

If we also reasonably assume $\beta \propto M^{-\nu}$ one finds that the boron isotope exponent, $\alpha_B = -\partial \ln T_c/\partial \ln M$ can be approximately written as

$$\alpha_B \simeq M \frac{\partial(\delta t/t^0)}{\partial M} = \frac{1}{2} \frac{\delta t}{t^0} - \nu \frac{\omega_D}{t^0} \frac{\partial}{\partial \ln u}\left(\frac{\delta t}{\omega_D}\right). \qquad (24)$$

In Eq. (24) the last term can be calculated from the Fig. 1. Since $\delta t/t^0 \sim 0.1$, and the derivative of $\delta t/\omega_D$ with respect to u is negative, α_B has a positive but small value. The isotope exponent as a function of the dimensionless squeezing parameter η/ω_D^2 is presented in the Fig. 2 for $\nu=1$. At the value of the squeezing parameter where the ground-state energy is minimum (i.e. $\eta/\omega_D^2 \sim 0.04-0.05$) the isotope exponent yields $\alpha_B \sim 0.25-0.30$ which is very close to the experimental value $\alpha_B \sim 0.27$ [9].

Acknowledgement

References

[1] C. Mazumdar, R. Nagarajan, G. Godart et al., Solid State Commun. 87 (1993) 413.

[2] R. Nagarajan et al., Phys. Rev. Lett. 72 (1994) 274.

[3] R.J. Cava et al., Nature (London) 367 (1994) 146.

[4] R.J. Cava et al., Nature (London) 367 (1994) 252.

[5] T. Siegrist, H.W. Zandbergen et al., Nature (London) 367 (1994) 254.

[6] L.F. Mattheiss, T. Siegrist and R.J. Cava, Solid State Commun. 91 (1994) 587.

[7] L.F. Mattheiss, Phys. Rev. B 49 (1994) 13279.

[8] M.S. Golden, M. Knupfer, M. Kielwein et al., Europhys. Lett. (1994), to be published.

[9] D.D. Lawrie and J.P. Franck, to be published in Physica C: Proceedings of M²S-HTSC-IV, Grenoble, France, ed. P. Wyder (Elsevier 1994).

[10] T. Hakioğlu, V.A. Ivanov, A.S. Shumovsky and B. Tanatar, to be published in Physica C: Proceedings of M²S-HTSC-IV, Grenoble, France, ed. P. Wyder (Elsevier 1994).

[11] S. Ishihara, T. Egami and M. Tackiki, Phys. Rev. B 49 (1994) 8944.

[12] M.L. Kulić and R. Zeyher, Phys. Rev. B 49 (1994) 4395.

[13] N.M. Plakida, in: Electron–Phonon Interaction in Oxide Superconductors, Proc. First CINVESTAV Superconductivity Symp., ed. R. Baquero (World Scientific, Singapore, 1991).

[14] H. Zheng and K. Nasu, Phys. Rev. B 45 (1992) 2148.

[15] H. Zheng, Phys. Rev. B 38 (1988) 11865.

[16] B. Chakraverty, D. Feinberg, Z. Hang and M. Avignon, Solid State Commun. 64 (1987) 1147.

[17] M. Hiratsuka, T. Sota and H. Suzuki, Proc. Ann. Meeting of Phys. Soc. Jpn., Fukuoka, 1994, vol. 3, p. 330.

[18] Z. Kakol, J. Spalek and J.M. Honig, J. Solid State Chem. 79 (1989) 288.

[19] J. Acrivos, J. Solid State Chem. (1994), to be published.

[20] V.A. Ivanov, Sov. J. Inorg. Chem. 34 (1989) 3201.

[21] V.A. Ivanov, in: Studies of High Temperature Superconductors, vol. 11, ed. A. Narlikar (Nova Science, New York, 1993).

[22] V.A. Ivanov, J. Phys. Condens. Matter 6 (1994) 2065; Physica B 186 (1993) 921.

[23] A. Bedyaev, V.A. Ivanov and V.E. Shilov, Theor. Math. Phys. 64 (1985) 163.

[24] V.A. Ivanov, Physica C 162 (1989) 1485.

[25] V.A. Ivanov and R.O. Zaitsev, Int. J. Mod. Phys. B 3 (1989) 1403.

[26] H. Takagi, H. Eisaki, S. Uchida et al., in: Proc. Ann. Meeting of Phys. Soc. Jpn., Fukuoka, 1994, vol. 2, p. 417.