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SYMMETRY BREAKING, NON-ADIABATIC ELECTRON-PHONON COUPLING AND NUCLEAR KINETIC EFFECT ON SUPERCONDUCTIVITY OF MgB₂

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Abstract: Theory of non-adiabatic electron-vibration interactions has been applied to the study of MgB₂ superconductivity. It has been shown that at the non-adiabatic conditions when the Born-Oppenheimer approximation is not valid, and electronic motion is dependent not only on the nuclear coordinates but also on the nuclear momenta, the fermionic ground state energy of some systems can be stabilised by electron-phonon interactions at broken translation symmetry and an energy gap in one-particle metallic spectrum can be opened. More over, the new arising state is geometrically degenerate – i.e., there is an infinite number of different nuclear configurations with the same fermionic ground state energy. The superconducting state transition can be characterised as a Non-Adiabatic Sudden Increase of the Cooperative Kinetic Effect at Lattice Energy Stabilization (NASICKELES). Comparing to the experiments, the model study of MgB₂ yields very good results. Calculated T_c is 39.5 K, and density of states exhibits two-gap character in full agreement with the tunneling spectra. The peaks are at +/-4 meV that is connected to π band and at +/-7.6 meV for σ band

1. INTRODUCTION

Comparable values of the Fermi energy and energy of the relevant vibration/phonon mode(s), i.e. $E_F \approx \omega$, indicate that electronic and nuclear motions are mutually dependent and cannot be studied as statistically independent fields. Consequently, separation of the electronic and nuclear motions by means of the Born – Oppenheimer (BO) approximation (or application of Migdal theorem to a theory of superconducting state transition) with the correction to the electronic energy over the diagonal part of the nuclear energy term (diagonal BO correction – DBOC) and corrected nuclear potential energy, i.e. adiabatic approximation, is for such systems incorrect.

It means that standard field theory Hamiltonian of the form,

$$H = H_{ce} + H_{ph} + H_{int} \approx \sum_k \varepsilon_k a_k^\dagger a_k + \sum_v \hbar \omega_v (b_v^\dagger b_v + \frac{1}{2}) + H_{int}(a^\dagger a, b^\dagger b)$$

is an inadequate starting point for correct description of such systems.

1.1 Non-adiabatic treatment of electronic structure calculation

Starting Hamiltonian is written in the general form of nonrelativistic – “chemical” Hamiltonian of interacting set of atoms ,

$$H = T_N(P) + E_{NN}(Q) + \sum_{PQ} h_{PQ}(Q) a_P^\dagger a_Q + \frac{1}{2} \sum_{PQRS} v_{PQRS}^0 a_P^\dagger a_Q^\dagger a_S a_R \quad (1)$$

The Hamiltonian is an explicate function of the operators of nuclear coordinates, \bar{Q}_V , and nuclear momenta, \bar{P}_V : $\bar{Q}_V = (\bar{b}_V^\dagger + \bar{b}_V)$, $\bar{P}_V = (\bar{b}_V - \bar{b}_V^\dagger)$

The terms, $E_{NN}(\bar{Q})$ and $h_{PQ}(\bar{Q})$ are introduced over the Taylor’s expansion at the equilibrium geometry of fixed nuclear configuration R_0 (crude level – clamped nuclei),

$$E_{NN}(\bar{Q}) = E_{NN}^0(eq) + \sum_{i=1}^{\infty} E_{NN}^{(i)}(\bar{Q}) \quad , \quad h_{PQ}(\bar{Q}) = h_{PQ}^0 + \sum_{i=1}^{\infty} u_{PQ}^{(i)}(\bar{Q})$$

$$u_{PQ}(\bar{Q}) = \left\langle P \left| \sum_j \frac{-Z_j e^2}{|r - R_j|} \right| Q \right\rangle^* f(\bar{Q})$$

The term $E_{NN}^0(eq)$ is the potential energy of the clumped nuclei configuration at the equilibrium geometry R_0 (crude level), h_{PQ}^0 is one – electron term (“core” Hamiltonian) for equilibrium nuclear configuration R_0 , and $u_{PQ}(\bar{Q})$ represents matrix element of electron – vibration (phonon) coupling.

The problem introduced by this Hamiltonian is studied by means of the unitary – canonical quaziparticle transformation technique in two steps [1],

1st. step: adiabatic, Q-dependent transformation,

$$\bar{H}_a = e^{-S_1(Q)} H e^{S_1(Q)} \tag{2}$$

2nd. step: non-adiabatic, P-dependent transformation,

$$H_{na} = e^{-S_2(P)} \bar{H}_a e^{S_2(P)}, \tag{3}$$

with subsequent iterative solution of the resulting coupled set of SCF-HF, GCPHF (generalized coupled perturbed Hartree-Fock, which mix electronic and nuclear motion) and nuclear secular equations. The procedure is connected to geometry optimization of the system with respect to the total energy of system.

The solution yields [1], beside the final set of normal modes frequencies, the final nonadiabatic form of the fermionic Hamiltonian, that is:

$$H_F = H_A(crude) + \Delta H_F \tag{4}$$

In this equation, $H_A(crude)$ is the clamped nuclei (crude – BO level) Hamiltonian,

$$H_A(crude) = H_{A^0(0)} + H_{A^1(0)} + H_{A^2(0)} \tag{5}$$

where $H_{A^0(0)}, H_{A^s(0)}, H_{A^{ss}(0)}$ are: zero-particle term (clumped nuclei fermionic ground state energy), one-particle Hamiltonian (one-particle spectrum - orbital energies) and two-particle Hamiltonian (correlation energy). The non-adiabatic corrections to the electronic energy are represented by the term ΔH_F ,

$$\Delta H_F = \Delta H_F^0 + \Delta H_F^1 + \Delta H_F^2 \quad (6)$$

with the corresponding corrections to zero, one and two – particle terms. Under the assumption of the dominance of electron–nuclear interaction (one-particle terms) at the coupling of the electron-nuclear motion, an approximate analytic solution of the GCPHF equations [1] for adiabatic Q-dependent (C_{PQ}^r) and non-adiabatic P-dependent (\hat{C}_{PQ}^r) unitary transformation coefficients is:

$$C_{PQ}^r = U_{PQ}^r \frac{(\varepsilon_P^0 - \varepsilon_Q^0)}{(\hbar w_r)^2 - (\varepsilon_P^0 - \varepsilon_Q^0)^2}; \hat{C}_{PQ}^r = U_{PQ}^r \frac{\hbar w_r}{(\hbar w_r)^2 - (\varepsilon_P^0 - \varepsilon_Q^0)^2}$$

The basic equations of the nonadiabatic corrections to electronic energy are:

1. Ground – state energy correction (real - space orbital representation),

$$\Delta H_F^0 = \Delta E_F^0 = \sum_{Alr} \hbar w_r (|C_{Al}^r|^2 - |\hat{C}_{Al}^r|^2) = \sum_{Al} \Omega_{Al} \quad (7)$$

{A} – unoccupied molecular orbitals, {I} – occupied molecular orbitals,
{r} – normal modes, with Ω_{PQ} being a symmetric matrix,

$$\Omega_{PQ} = \sum_r \hbar w_r (|C_{PQ}^r|^2 - |\hat{C}_{PQ}^r|^2) = \sum_r \hbar w_r \frac{|U_{PQ}^r|^2}{(\varepsilon_P^0 - \varepsilon_Q^0)^2 - (\hbar w_r)^2} = \Omega_{QP}$$

For k – space representation this equation reads,

$$\Delta H_F^0 = \Delta E_F^0 = 2 \sum_{k,k'} |U^{k-k'}|^2 f_k (1 - f_{k'}) \frac{\hbar w_{k-k}}{(\varepsilon_{k'}^0 - \varepsilon_k^0)^2 - (\hbar w_{k-k})^2} \quad (8)$$

2. One – particle energy correction:

a) Correction to the orbital energies (part of the one-particle correction that influence shift of the orbital energies with respect to E_F - i.e. boson operators independent part). The real space orbital representation is,

$$\Delta H'_F = \sum_P \Delta \varepsilon_P N[a_P^\dagger a_P] = \sum_P (\sum_A \Omega_{PA} - \sum_I \Omega_{PI}) N[a_P^\dagger a_P] \quad (9)$$

b) The total one-particle corrections due to nonadiabatic electron- vibration interactions (includes the above boson-independent contribution and boson dependent part – expression below is for boson vacuum):
k – space representation (“dressed polarons”),

$$\begin{aligned} \Delta H'_F = & \sum_{k,q,\sigma} |U^q|^2 \frac{1}{(\varepsilon_k^0 - \varepsilon_{k-q}^0) - \hbar\omega_q} N[a_{k,\sigma}^\dagger a_{k,\sigma}] - \\ & - 2 \cdot \sum_{k,q,\sigma} |U^q|^2 f_{k-q} \frac{\hbar\omega_q}{(\varepsilon_k^0 - \varepsilon_{k-q}^0)^2 - (\hbar\omega_q)^2} N[a_{k,\sigma}^\dagger a_{k,\sigma}] \end{aligned} \quad (10)$$

In this expression, the first term is basically an energy of single polaron (“Lee – Low – Pines” polaron) and the second term is an energy correction to a polaron energy due to SCF field of all other polarons.

3. Two - particle energy correction: correction to electron – electron correlation energy due to the phonon field. This non-adiabatic term represents full attractive contribution, and can be compared to the reduced form of Fröhlich effective Hamiltonian which maximizes attractive contribution of electron – electron interaction and that can be either attractive or repulsive (interaction term of the BCS theory). For superconducting state transition at the non-adiabatic conditions, the two-particle correction is unimportant – see [2].

2. NON-ADIABATIC EFFECTS IN MgB₂: RESULTS

The non-adiabatic theory indicates that electron - vibration (phonon) interaction, at stabilization (minimization) of the fermionic ground state

energy, can induce nuclear displacements out-of the original equilibrium configuration R_0 , i.e. to break the original translation symmetry [3]. At these circumstances, it is necessary to investigate if for MgB_2 there exists a distorted structure that is more stable, due to non-adiabatic EP interactions, than the original equilibrium structure, and look for possibility of some other than BCS mechanism at the transition to superconducting state.

2.1 Band structures of MgB_2

Presented band structure calculations have been done by computer code SOLID 2000 [4,5]. The lattice parameters of MgB_2 (hexagonal structure, space group $P6mm$), with the fraction coordinates of the unit cell atoms: $\text{Mg} = (0,0,0)$; $\text{B1} = (1/3,2/3,1/2)$; $\text{B2} = (2/3,1/3,1/2)$, have been optimized in a good agreement with the experiment.

a/ Equilibrium – undistorted geometry

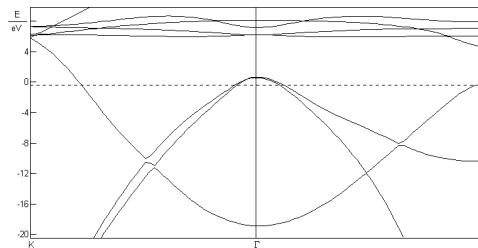


Figure II:2:1. Band structure of MgB_2 calculated at the equilibrium – undistorted geometry - details for the path K- Γ -M. The Fermi level - E_F is indicated by the dashed line.

b/ Distorted geometries

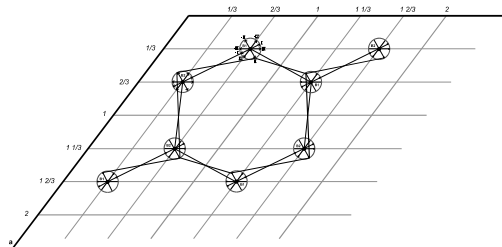


Figure II:2:2. undistorted high symmetry structure of B atoms in $\mathbf{a-b}$ plane and symmetry breaking by the in-plane, out-of phase displacements $|\Delta f|/\text{atom}$. The motion of B1-B2 atoms in out-of phase positions along the perimeters of circles with radius Δf centred at the undistorted B atoms positions generates an infinite number of distorted structures. The figure

indicates beside the undistorted structure also one of the distorted structures that correspond to the E_{2g}(b) phonon mode distortion (bold line).

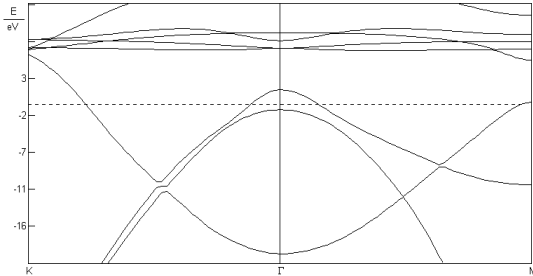


Figure II:2:3. Band structure of MgB₂ calculated for the distorted geometry. The displacement of B atoms is $|\Delta f| = 0.005/\text{atom}$ (fraction unit) that correspond to 0.032 Å of B1-B2 bond length elongation for stretching vibration (E_{2g}(a) phonon mode amplitude). At this displacement, the lower splitoff σ band has just sank below E_F. The Fermi level - E_F is indicated by the dashed line. The band structure calculations indicate that dominant is σ_1 - σ_2 and σ_1 - π bands coupling over the E_{2g} phonon mode.

2.2 Deformation energy

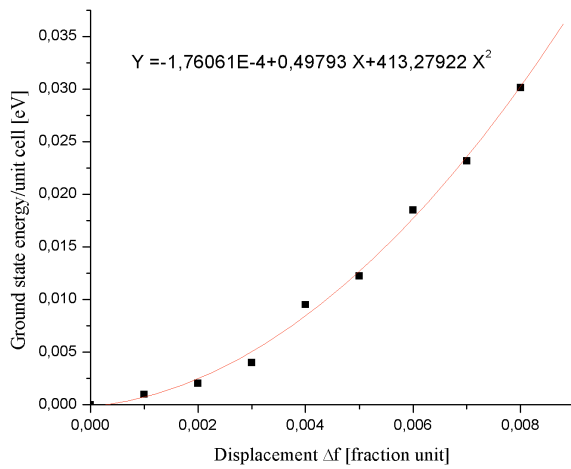


Figure II:2:4. The MgB₂ electronic ground state energy/unit cell as the function of the displacement Δf . The electronic energy of the undistorted structure is the reference value - 0 eV. The dependence is harmonic over the studied range of the displacements, and is identical

for all studied types of the distortions. At the displacement $|\Delta f| = 0.005/\text{atom}$, the lower splitoff σ band has just sank below E_F , and the ground state energy has been destabilized by 12 meV.

2.3 Non-adiabatic correction to zero – particle term of the fermionic Hamiltonian. Correction to the fermionic ground state energy

The study of the E_{2g} phonon mode dispersion [6] indicates different frequencies at Γ and K points, $\hbar\omega_\Gamma \approx 0.066$ eV, and $\hbar\omega_K \approx 0.090$ eV. In this case, for the fermionic ground state energy correction holds,

$$\begin{aligned} \Delta H_F^0 = \Delta E_F^0 = VP \int_{z_{\min}}^{z_{\max}} \left| U_{z,\Gamma}^{(E_{2g})} \right|_{\sigma-\sigma}^2 n_{z,\sigma} \frac{\hbar\omega_\Gamma}{z^2 - (\hbar\omega_\Gamma)^2} dz \\ + VP \int_{z_{\min}}^{z_{\max}} \left| U_{z,K}^{(E_{2g})} \right|_{\sigma-\pi}^2 n_{z,\pi} \frac{\hbar\omega_K}{z^2 - (\hbar\omega_K)^2} dz \end{aligned} \quad (11)$$

with z being, $z = (\varepsilon_A^0 - \varepsilon_I^0)$, i.e., the difference of the orbital energies of interacting pairs of unoccupied states $\{\varepsilon_A^0\}$ and occupied states $\{\varepsilon_I^0\}$ of the particular clumped nuclear structure. Integration in above equation runs from $z_{\min} = \hbar\omega_r/q$ up to $z_{\max} \gg \hbar\omega_r (= \infty)$. The quantity “ q ” ($q \geq 1$) in z_{\min} “regulates” the distance of the top of the lower splitoff σ band from E_F . The quantity n_z represents „density“ for energy differences z of the interacting pairs of states. The matrix element of EP coupling for phonon mode r , $U_z^{(r)}$, is also z -dependent.

$$\bar{U}_{\sigma-\sigma} = \left\langle U^{(E_{2g})} \right\rangle_{\sigma-\sigma} \approx 0.7 \text{ eV}, \text{ for } \sigma-\sigma \text{ bands interaction, and}$$

$$\bar{U}_{\sigma-\pi} = \left\langle U^{(E_{2g})} \right\rangle_{\pi-\sigma} \approx 0.25 \text{ eV}, \text{ for } \pi-\sigma \text{ bands interaction.}$$

The ground state energy loss (destabilization) due to symmetry distortion, for the displacement $|\Delta f| = 0.005$, when the top of the lower splitoff σ band has approached, crossed E_F and sank just below it, has been calculated to be

+12 meV/unit cell (see Fig. 4). For this value of the displacement, the ground state energy correction due to non-adiabatic EP coupling is about -50 meV (Fig.6.,q = 2). Due to k : (-k) symmetry, this figure has to be multiplied by 2, and actual figure for q = 2 is 98.8 meV The net effect of the distortion – symmetry lowering is the fermionic ground state energy stabilization.

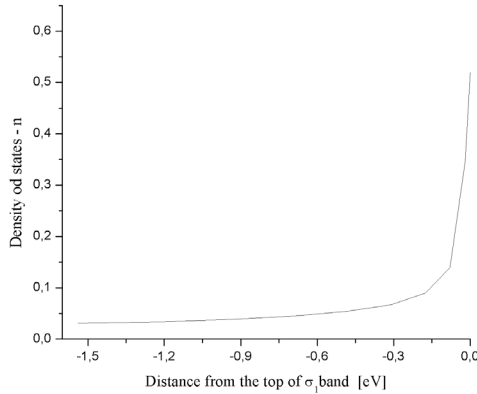


Figure II:2:5. Dependence of the σ_1 band density of states on the energy distance from the top of the band. For the relevant energy interval $\approx \hbar\omega_\Gamma$, the approximate mean value $n_{\sigma_1} = 0.2$ has been used. Outside of this interval, the density rapidly falls and reaches the value nearly ten times smaller, 0.03. For the upper σ band, the density of unoccupied states and occupied states at E_F are $n_{A(I)} = 0.02$. Density of unoccupied and occupied states of π band at E_F are calculated to be basically the same, $n_{B(J)} = 0.02$.

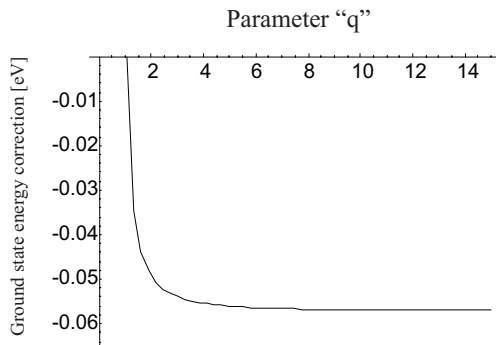


Figure II:2:6. The non-adiabatic correction to the fermionic ground state energy/unit cell of the MgB₂ as the function of the parameter “q” – see text. For q=2, it is -49.4 meV.

It means that due to effective non-adiabatic EP coupling, the distorted structure for a displacement of $|\Delta f| \approx 0.0045 - 0.005$ ($0.016 \text{ \AA}/\text{atom}$) is by $(-98,8 + 12) = -86,8$ meV more stable than undistorted – equilibrium structure on the BOA level. More over, this new – nonadiabatic ground state is geometrically degenerate. There are an infinite number of the B-B atoms in plane, out-of-phase displacements (see Fig.2), i.e. there can exist different nuclear configurations with the same ground state energy. On the lattice scale, geometrical degeneracy of the fermionic ground state energy for distorted structure, i.e. existence of an infinite number of out-of-phase B-B atoms displacements, enables cooperative and dissipationless motion of out-of-phase displaced B-B atoms along the perimeters of circles centered at the undistorted B-B atoms positions, with the same radii equal to the fraction displacement $|\Delta f| \approx 0.0045 - 0.005$ ($\approx 0.016 \text{ \AA}$). This is a new, coherent macroscopic quantum state.

2.4 Non-adiabatic correction to the one-particle term of the fermionic Hamiltonian. Corrections to the orbital energies and gap opening in a metallic one-particle spectrum.

For nonadiabatic correction, $\Delta \varepsilon_I$, to an occupied state ε_I^0 holds,

$$\Delta \varepsilon_I = \sum_A^{occ} \Omega_{IA} - \sum_J^{occ} \Omega_{IJ} \quad (12)$$

In case of MgB₂, for quazicontinuum of states, with incorporation of the Lorenz line-shape form of the phonon mode, one can write:

$$\Delta \varepsilon_I = \frac{d}{\pi} \int_{-\infty}^{\infty} \frac{dx}{(x - \hbar\omega)^2 + d^2} \int_0^{\hbar\omega/q} n_B |U_{BI}|^2 \frac{x}{(\varepsilon_I^0 - \varepsilon_B^0)^2 - (x)^2} d\varepsilon_B^0 \quad (13)$$

The original state ε_I^0 (orbital energy of the occupied state for particular clumped nuclear structure) is by this correction shifted on the energy scale to a new position,

$$\mathcal{E}_I = \mathcal{E}_I^0 + \Delta\mathcal{E}_I \quad (14)$$

For non-adiabatic correction, $\Delta\mathcal{E}_A$, to an unoccupied state \mathcal{E}_A^0 holds,

$$\Delta\mathcal{E}_A = \sum_B^{unocc} \Omega_{AB} - \sum_J^{occ} \Omega_{AJ}, \quad (15)$$

In case of MgB₂, for quazicontinuum of states, with incorporation of the Lorenz line-shape form of the phonon mode, holds :

$$\Delta\mathcal{E}_A = -\frac{d}{\pi} \int_{-\infty}^{\infty} \frac{dx}{(x - \hbar\omega)^2 + d^2} \int_{-\infty}^{-|\hbar\omega/q|} n_J |U_{AJ}|^2 \frac{x}{(\mathcal{E}_A^0 - \mathcal{E}_J^0)^2 - (x)^2} d\mathcal{E}_J^0 \quad (16)$$

and the original state \mathcal{E}_A^0 (orbital energy of the unoccupied state for particular clumped nuclear structure) is shifted to a new position,

$$\mathcal{E}_A = \mathcal{E}_A^0 + \Delta\mathcal{E}_A \quad (17)$$

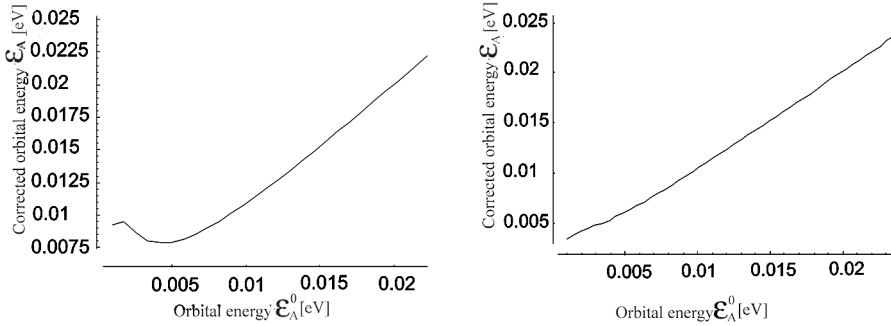


Figure II.2:7. The orbital energies of the unoccupied states after the non-adiabatic corrections (shifts) v.s. the original-uncorrected orbital energies of the σ_2 band (left) and π band (right). The minimum on the graphs indicates the energy position of the lowest unoccupied state of the σ_2 band (left) and π band (right) with respect to $E_F (=0)$.

From the Figs.7. one can see that after the non-adiabatic corrections, the energy distance of the lowest unoccupied state from the E_F (half-gap) is 7.6 meV for σ_2 band and 4 meV for π band. According to the gap equation [7],

$$\Delta(T) = \Delta(0) \tanh \frac{\Delta(T)}{4k_B T} \quad (18)$$

calculated value of the critical temperature T_c is: $T_c(\sigma_2) = 39.5$ K for σ_2 band gap, and $T_c(\pi) = 20.8$ K for π band gap.

2.5 Non-adiabatic corrections to the density of states

For the final density of states that account for the effect of non-adiabaticity, the following equation can be derived [8]:

$$n(\varepsilon_Q) = \frac{1}{\left| 1 + \frac{\partial(\Delta\varepsilon_Q)}{\partial\varepsilon_Q^0} \right|} n(\varepsilon_Q^0) \quad , \quad (19)$$

with , $\Delta\varepsilon_Q = \varepsilon_Q - \varepsilon_Q^0$, and $n(\varepsilon_Q^0) = \left(\left(\frac{\partial\varepsilon_Q^0}{\partial k} \right)^{-1} \right)$

3. CONCLUSION

The non-adiabatic theory of EP interactions offers substantially different scenario of SC state transition than BCS one (or pairing theories in general). At stabilization of SC state, instead of Cooper pairs formation and Bose condensation at equilibrium geometry of clumped nuclei BOA structure, at the non-adiabatic level the crucial is symmetry breaking (nuclear displacements) resulting in a lower symmetry structure with the fermionic ground state energy geometrical degeneracy of atoms displacements and with the new one-particle spectrum that maximize non-adiabatic EP interactions. Meaning of the gap is also different here. In the non-adiabatic

case, the gap has its usual meaning, i.e. quaziparticle (“non-adiabatic polaron”) excitation energy over the one-particle spectrum.

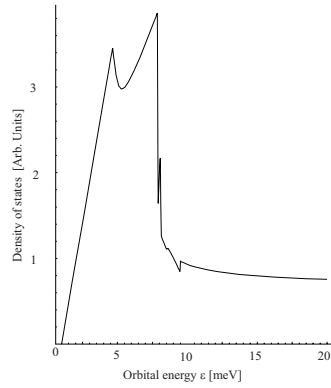


Figure II:2:8. The final – non-adiabatic density of the unoccupied states at 0 K, according to Eq.19. The uncorrected density of states is normalized to 1 and $E_F = 0$. The peak at 4 meV corresponds to non-adiabatic corrections of π band states and the peak at 7.6 meV corresponds to non-adiabatic corrections of σ_2 band states. The density of the occupied states is the mirror picture with respect to E_F .

At finite temperatures, with increasing temperature from 0 K, due to Fermi statistics of the one-particle state populations, the non-adiabatic EP corrections become smaller (T-dependent contribution), and at crossing critical temperature T_c , the electronic energy loss due to symmetry lowering (T-independent contribution) becomes greater than the energy gain due to nonadiabatic EP interactions. The system, in order to minimize fermionic ground state energy, goes to normal – metal state with the “equilibrium“ geometry of the higher symmetry. For cooling, the situation is opposite. At crossing T_c in downward direction, the distorted structure becomes more stable than the undistorted one. The reason is that at lowered symmetry, there is the proper structure of the one-particle spectrum at E_F , the structure that effectively enables to switch-on and maximizes the non-adiabatic EP interactions. The non-adiabatic energy gain starts to prevail over the energy loss of the distortion.

The SC state transition can be characterized as a non-adiabatic sudden increase of the cooperative kinetic effect at lattice energy stabilization (NASICKELES). It is exactly participation of the nuclear kinetic energy

term on the non-adiabatic level that stabilize (negative contribution) fermionic ground state energy at a distorted structure. At the adiabatic conditions, nuclear kinetic effect is absent, and adiabatic correction (DBOC - effect of nuclear positions) to the fermionic ground state energy is always positive for equilibrium as well as for distorted clumped nuclei structures. It should be pointed out that for undistorted – equilibrium structure, the one-particle spectrum is of such character that non-adiabatic EP interactions do not contribute to the ground state energy stabilization. Only at the lowered symmetry – distorted structure, when the orbital energies are shifted into the “right” positions at E_F (formation of the new one-particle spectrum after distortion), the non-adiabatic EP interactions can become operative and effective. Geometrical degeneracy of the fermionic ground state energy for distorted structure, i.e. existence of an infinite number of out of phase B-B atoms displacements, enables cooperative motion (cooperative nuclear microcirculations) of out-of-phase displaced B-B atoms along the perimeters of circles centered at the undistorted B-B atoms positions, with the same radii equal to the fraction displacement $|\Delta f|$.

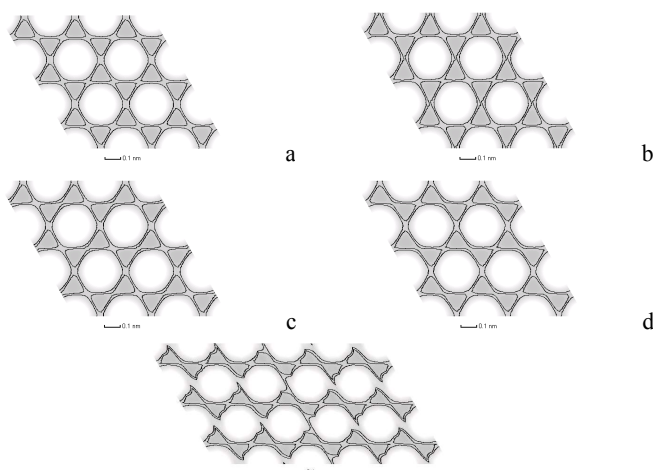


Figure II:2:9a-e. The valence electron iso-density lines in the plane of B atoms (**a-b** plane) for equilibrium (**a**) and distorted structures (**b-e**). The electron density is localized at B atom positions for equilibrium structure (**a**). The B atoms displacements ($|\Delta f| = 0.005$) induce the alternating interatomic charge density delocalization, different for the particular types of the distortion (**b-d**). Nuclear “microcirculation” enables then effective charge transfer over the lattice in an external electric potential. The Fig (**e**) corresponds to the case of the distortion (**d**) over the larger lattice segment.

In the present case, the radius of circles is $|\Delta f| = 0.005$ (expressed in fraction unit), that is 0.016 \AA° in the absolute value. The cooperative nuclear motion, i.e. “nuclear microcirculations”, induces dynamic - cooperative formation of shortened and elongated in-plane B-B bond distances on the lattice scale, with a dynamic formation of increased and decreased interatomic charge densities – see Fig 9a-e, i.e. dynamic formation of non-adiabatic bipolarons.

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