Supplemental Material to the article „Insulator-bad metal transition in $RNiO_3$ nickelates beyond Hubbard model and density functional theory“

I. Effective field theory: Atomic limit. Within molecular field approximation (MFA) the bilinear Hamiltonian of nonlocal charge correlations reads as follows:

$$\frac{1}{2}\sum_{i\neq j} V_{ij}\hat{\Sigma}_{zi}\hat{\Sigma}_{zj} \simeq \frac{1}{2}\sum_{i\neq j} 2V_{ij}\hat{\Sigma}_{zi}\langle\hat{\Sigma}_{zj}\rangle - \frac{1}{2}\sum_{i\neq j} V_{ij}\langle\hat{\Sigma}_{zi}\rangle\langle\hat{\Sigma}_{zj}\rangle$$

$$= -\sum_i h_i\hat{\Sigma}_{zi} - \frac{1}{2}\sum_{i\neq j} V_{ij}\langle\hat{\Sigma}_{zi}\rangle\langle\hat{\Sigma}_{zj}\rangle\,, \qquad (S1)$$

where

$$h_i = -\sum_{j\neq i} V_{ij}\langle\hat{\Sigma}_{zj}\rangle \qquad (S2)$$

is the molecular field, $\langle ...\rangle$ is a thermodynamical average. The last term in $(S1)$ depends entirely on pseudospin averages, however, this term must be carefully taken into account when calculating free energy.

Thus, the effective Hamiltonian can be represented as a sum of on-site contributions. In the two-sublattice (A and B) approximation

$$\mathcal{H}_0 = \sum_{c=1}^{N/2}\mathcal{H}_c, \qquad \mathcal{H}_c = \mathcal{H}_A + \mathcal{H}_B\,, \qquad S3$$

where without taking into account the electron-lattice interaction

$$\mathcal{H}_\alpha = \frac{U}{2}\hat{\Sigma}^2_{z\alpha} - h_\alpha\hat{\Sigma}_{z\alpha}\,, \qquad (S4)$$

$\alpha = A, B$,

$$h_{A,B} = -zV\langle\hat{\Sigma}_{zB,A}\rangle \qquad (S5)$$

are molecular fields, $z=6$ is the number of nearest neighbors, V is the parameter of nonlocal nn-interactions. Note that, taking into account the "non-operator" term in the Hamiltonian of nonlocal correlations (the last term in $(S1)$) the energy of the "disproportionated" states of the octet with $|M|=1$ should be increased by $\frac{1}{2}zV$. Thus, the ground state of the octets corresponds to the Jahn-Teller configuration at $zV < U$ and the classical "disproportionated" CO-configuration at $zV > U$, in which the centers M = +1 ([the spin-0 $NiO_6]^{8-}$ cluster) and M = -1 (the spin-1 $[NiO_6]^{10-}$ cluster) occupy the corresponding sublattices. At $zV = U$ the energies of the configurations coincide. It is interesting that the Hamiltonian $\mathcal{H}_\alpha$ resembles the Hamiltonian of the spin $S=1$ center with axial single-ion anisotropy of the "easy plane" type, in an external field directed along the symmetry axis.

The octet distribution function reads as follows

$$Z_c = \mathrm{Tr}\left(e^{-\beta\mathcal{H}_c}\right) = \mathrm{Tr}\left(e^{-\beta\mathcal{H}_A}\right)\ \mathrm{Tr}\left(e^{-\beta\mathcal{H}_B}\right) = Z_A Z_B\,,$$

where $\beta = 1/k_BT$,

$$Z_{A,B} = 4 + e^{-\frac{1}{2}\beta U}(3e^{-\beta h_{A,B}} + e^{\beta h_{A,B}})\,. \qquad (S6)$$

The free energy per center takes the form

$$f = -\frac{1}{2\beta}(\ln Z_A + \ln Z_B) - \frac{1}{2}zV(\Delta n^2 - l^2)\,. \qquad (S7)$$

By minimizing the free energy, we can obtain equations for determining the order parameters.

For illustration, Fig. $S1$ shows the dependence of the free energy on the order parameter l for different temperatures and different values for the parameter V in units of $U > 0$.

II. Effective field theory: Two-electron boson transport. In contrast to the atomic limit with the essentially classical effect of nonlocal inter-site correlations, the introduction of a molecular field to describe the quantum effect of the two-particle charge transfer (quantum tunneling) seems to be a rougher approximation, but, we hope, not devoid of the potential for qualitative and semi-quantitative predictions.

In the framework of molecular field theory, we represent the transport Hamiltonian $\hat{H}^{(2)}_{kin}$ with some fixed component of the traditional spin as follows

$$\hat{H}^{(2)}_{kin} = -t_b\sum_{i\neq j}\left(\hat{\Sigma}^2_{i+}\langle\hat{\Sigma}^2_{j-}\rangle + \hat{\Sigma}^2_{i-}\langle\hat{\Sigma}^2_{j+}\rangle\right) +$$

$$\frac{1}{2}t_b\sum_{i\neq j}\left(\langle\hat{\Sigma}^2_{i+}\rangle\langle\hat{\Sigma}^2_{j-}\rangle + \langle\hat{\Sigma}^2_{i-}\rangle\langle\hat{\Sigma}^2_{j+}\rangle\right)\,, \qquad (S8)$$

where for quantum mechanical averages

$$\langle\hat{\Sigma}^2_{i\pm}\rangle = \langle\delta|\hat{\Sigma}^2_{i\pm}|\delta\rangle = \frac{1}{2}sin2\alpha = \frac{1}{2}\sqrt{(1-\delta^2)}\,, \qquad (9)$$

where the angle α determines quantum charge superpositions

$$|\delta\rangle = cos\alpha\,|+1\rangle + sin\alpha\,|-1\rangle\,. \qquad (S10)$$

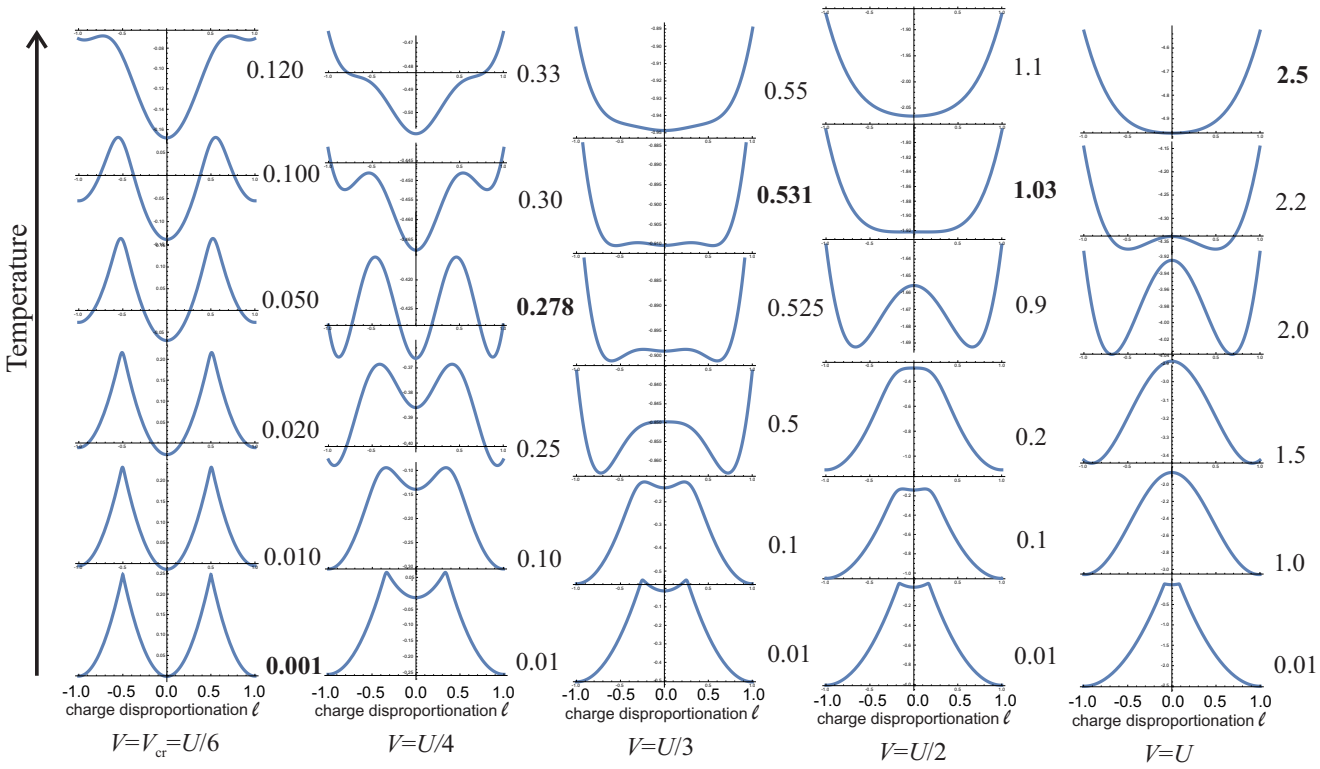

Fig. $S1$. Dependence of the free energy on the order parameter l for different temperatures given different values of the parameter V in units of $U>0$.

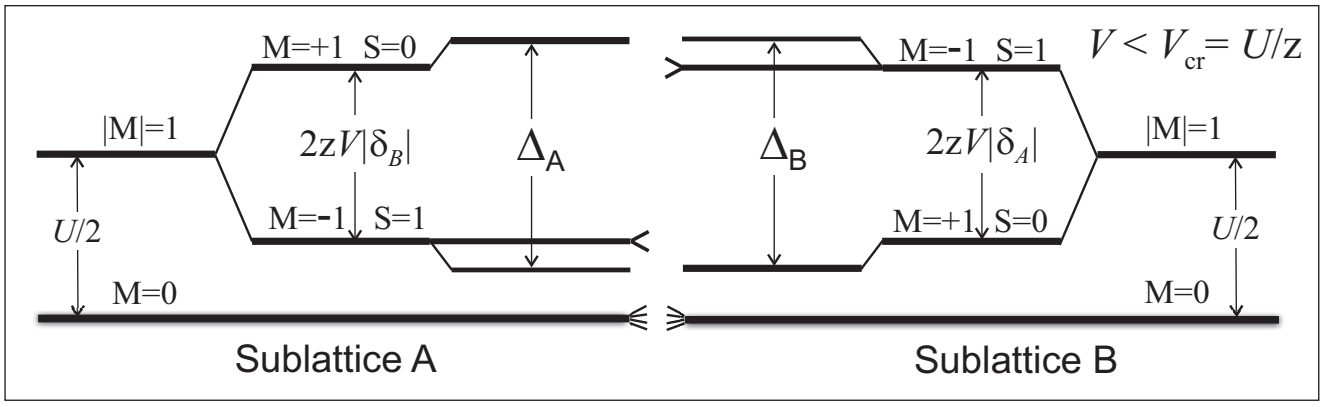

Fig. $S2$. Scheme of the energy spectrum of octets of NiO_6 clusters in two sublattices of model nickelate in the ground state, taking into account the pair transfer effect at $V < V_{cr}$.

In accordance with the effective field theory for the two-sublattice model, the operator part of the Hamiltonian ($S8$) is included in the Hamiltonian $\mathcal{H}_\alpha$ ($S4$), which leads to a modification of the energy spectrum of octets from two sublattices, shown in Fig. $S2$, where

$$\Delta_{A,B} = 2z\sqrt{V^2\delta^2_{B,A} + t_b^2(1-\delta^2_{B,A})} = 2z\sqrt{V^2\cos^2(2\alpha_{B,A}) + t_b^2\sin^2(2\alpha_{B,A})}\,. \quad (S11)$$

For the distribution functions $Z_{A,B}$ of octets in the sublattices we obtain

$$Z_{A,B} = 4 + e^{-\frac{1}{2}\beta U}(2e^{-\beta h_{A,B}} + 2\cosh\frac{\Delta_{A,B}}{2})\,. \quad (S12)$$

The free energy per center takes the form

$$f = -\frac{1}{2\beta}(\ln Z_A + \ln Z_B) + \frac{1}{2}zVl^2 + \frac{1}{4}zt_b(1-l^2)\,. \quad (S13)$$

As can be seen from the spectrum of the octet system (Fig. $S2$), in the limit of low temperatures, the quantum

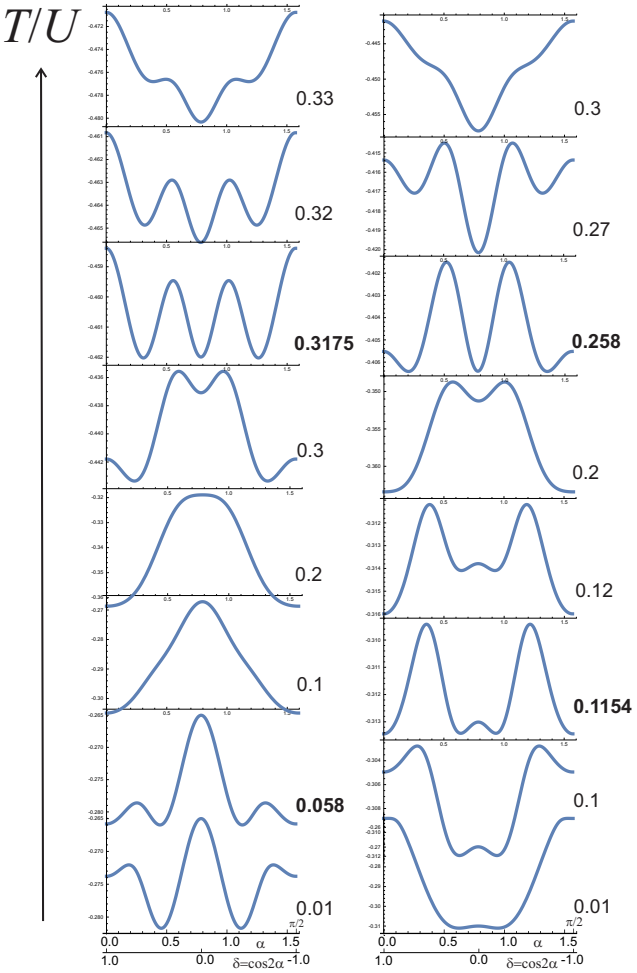

Fig. $S3$. The dependence of the free energy of the model nickelate on the angle α, which determines the composition of the quantum superposition ($S10$), or the order parameter $l = \cos 2\alpha$ at different temperatures given $V = 0.25\,U$, $t_b = 0.17\,U$ (left) and $t_b = 0.18\,U$ (right)

disproportionated CDq phase will be energetically favorable, although with increasing temperature the weight of the classical CO phase increases. The result of the competition of CDq, CO and NO phases is well illustrated in Fig. $S3$, that shows the dependence of the free energy of the model nickelate on the angle α, which determines the composition of the quantum superposition ($S10$), or the order parameter $l = \langle\langle \Sigma_z \rangle\rangle = \langle cos2\alpha \rangle$ at different temperatures given $V = 0.25\,U$, $t_b = 0.17\,U$ (left) and $t_b = 0.18\,U$ (right). As expected, in both cases the quantum CDq-phase turns out to be energetically more favorable, but with increasing temperature two first-order phase transitions CDq→CO and CO→NO are observed, and the CO-phase turns out to be stable in almost the entire range of ordering temperatures.

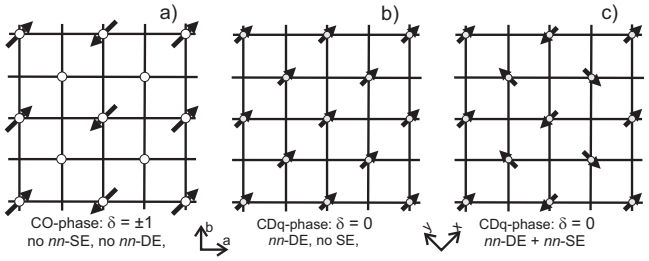

Fig. $S4$. Planar illustration of possible magnetic structures with $\mathbf{k} = (1/2,0,1/2)$ in orthonickelates: a) nickelate with classical charge disproportionation (CO phase), no nn-SE, no nn-DE ; b) nickelate with quantum charge disproportionation (CDq phase), nn-DE, no nn-SE ; c) nickelate with quantum charge disproportionation (CDq phase), nn-DE, nn-SE.

It is interesting that with a relatively small increase in the parameter t_b, a strong increase in the CDq–CO transition temperature is observed with a small but noticeable drop in the CO–NO transition temperatures, which, despite the large value of the parameter t_b, remain close to the value $T_{\rm CO} = 0.278$ characteristic of a system with $t_b = 0$ (see Fig. $S1$).

III. Briefly about the competition of bosonic double exchange (DE) and superexchange (SE) in nickelates. In Fig. $S4$a,b,c we present a simple planar illustration of possible magnetic structures in nickelates. In the CO phase (see Fig. $S4$a) both nn-SE and nn-DE are switched off, therefore, the phase is most likely paramagnetic. Fig. $S4$b presents a ferromagnetic (FM) structure for CDq phase due to only FM bosonic DE though FM structure is absolutely energetically unfavorable for antiferromagnetic (AFM) SE. However, the transition to the collinear AFM ordering actually corresponds to $S_{ij} \to 0$ and the transition to paramagnetic CO-phase with both the DE and SE contributions turned off. Strangely enough, the noncollinear structure (1/2,0,1/2) in ab-axes, or (1/4,1/4) in xy-axes (see Fig. $S4$c), arises as a result of a compromise between mutually exclusive pure AFM spin superexchange Ni^{2+}–Ni^{2+} and spin-charge bosonic double exchange, and spinless nonlocal correlations, that cannot be described in terms of an effective spin Hamiltonian.