The atomic-start description of NiO♠

R. J. Radwanski[*]

Center of Solid State Physics; S^{nt}Filip 5, 31-150 Krakow, Poland
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka

Center of Solid State Physics; S^{nt}Filip 5, 31-150 Krakow, Poland

We have calculated magnetic properties and the electronic structure of NiO both in the paramagnetic and in magnetically-ordered state as well as zero-temperature properties and thermodynamics within the strongly-correlated crystal-field approach. It is in agreement with a Mott's suggestion that NiO is an insulator due to strong electron correlations. We have quantified crystal-field, spin-orbit and magnetic interactions of the Ni^{2+} ion in NiO. We have obtained that $E_{dd} \gg E_{CF}(=2.0 \text{ eV}) \gg E_{s-o}(=0.29 \text{ eV}) \gg E_{mag}(=0.07 \text{ eV})$. The orbital moment of 0.54 μ_B amounts at 0 K, in the magnetically-ordered state, to about 20% of the total moment (2.53 μ_B). Our studies indicate that it is the highest time to "unquench" orbital magnetic moment in 3d solid-state physics and the necessity to take always into account strong intra-atomic correlations among d electrons and the intra-atomic spin-orbit coupling.

NiO attracts large attention of the magnetic community by more than 50 years. Despite of its simplicity (two atoms, NaCl structure, well-defined antiferromagnetism (AF) with T_N of 525 K) and enor-

* http://www.e-physica.pl; Email: sfradwan@cyf-kr.edu.pl

mous theoretical and experimental works the consistent description of its properties, reconciling its insulating state with the unfilled 3d band is still not reached [1–10].

The aim of this paper is to report the calculations of the magnetic moment, specific heat and the low-energy electronic structure of bulk NiO within the conventional ionic picture completed with inter-site spin-dependent interactions. We attribute this moment and this low-energy electronic structure to the Ni^{2+} ions in the rhombohedrally distorted NaCl structure. The approach used can be called the quasi-atomic approach as the starting point for the description of a solid is the consideration of the atomic-like electronic structure of the constituting atoms/ions. In the present case we start from the atomic-like electronic structure of eight electrons in the 3d shell of the Ni^{2+} in the oxygen octahedron. A macroscopic body of NiO with the NaCl structure is built up from such face-sharing octahedra.

We have treated the 8 outer electrons of the Ni^{2+} ion as forming the strongly-correlated atomic-like electron system $3d^8$. Its ground term is described by two Hund's rules yielding $S=1$ and $L=3$, i.e. the ground term ^3F [11]. In a solid such the localized strongly-correlated electron system interacts with the charge and spin surroundings. The charge surrounding has predominantly the octahedral symmetry owing to the NaCl-type of structure of NiO. Our Hamiltonian for NiO consists of two terms: the single-ion-like term H_d of the $3d^8$ system and the H_{d-d} intersite spin-dependent term. Calculations somehow resemble those performed for rare-earth systems, see e.g. Ref. [12] and they have been recently applied successfully to $3d$ compounds [10, 13]. For the calculations of electronic states of the quasi-atomic single-ion-like Hamiltonian of the $3d^8$ system we take into account the crystal-field interactions of the octahedral symmetry and the spin-orbit coupling (the octahedral CEF parameter B_4=+21 K (=+1.81 meV), the spin-orbit coupling constant λ_{s-o} = -480 K (= -41 meV) [11]). It is very important to know, that the positive sign of B_4 comes directly from *ab initio* calculations for the oxygen anion octahedral surroundings. We have chosen the value of B_4 of 21 K in order to reproduce experimentally observed an absorption peak at 1.06-1.13 eV [14], see also Fig. 5 of Ref. [8]. The single-ion states under the octahedral crystal field and the spin-orbit coupling have been calculated by consideration of the Hamiltonian [15]:

$$H_d = B_4(O_4^0 + 5O_4^4) + \lambda_{s-o}L \cdot S \qquad (1)$$

The charge-formed fine electronic structure, shown in Fig. 1, contains three groups of localized states. The higher groups are at 1.06-1.14 eV
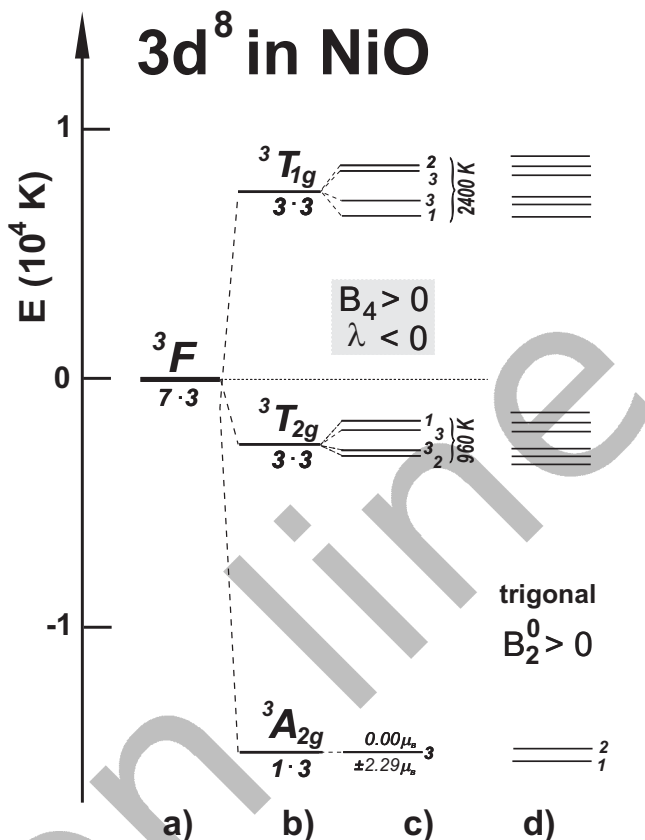
FIG. 1: The calculated fine electronic structure of the highly-correlated $3d^8$ electronic system in the paramagnetic state. a) the 21-fold degenerated ^3F term given by two Hund's rules: $S=1$ and $L=3$. b) the effect of the cubic octahedral crystal-field with $B_4=+21$ K. c) the combined action of the octahedral crystal field and the spin-orbit coupling with $\lambda_{s-o}= -480$ K. d) the effect of a trigonal distortion - the splitting of the ground triplet amounts to 12 K for $B_2^0= +50$K. The positive B_2^0 yields the singlet lower - such a situation is favored by the Jahn-Teller theorem.

and 1.91-2.05 eV. For low- and room-temperature properties the lowest triplet, originating from the cubic subterm $^3A_{2g}$, is the most important as the higher states are not thermally populated. The existence of this triplet in the spin-orbital space indicates that the Ni^{2+} ion is unstable

to lattice off-octahedral distortions, that splits the triplet. The value of $B_4 = +21$ K corresponds to another characteristics of the cubic crystal field Dq of 1260 K ($=875$ cm^{-1}). Historically for a configuration with a F ground term (d^2, d^3, d^7, d^8) the energy separation between $^3A_{2g}$ and $^3T_{2g}$ subterms is denoted as 10Dq. It should be noted that in theoretical approaches different values for 10Dq are considered like only 0.5 eV in Ref. [2, 5]. For getting the proper insulating gap an enormous splitting between spin-up and spin-down e_g states of 10.8 eV was introduced in Ref. [4], that according to us is not physically justified.

For the description of the trigonal distortion observed in NiO the cubic Hamiltonian (1) is necessary to transform in order to have the z quantization axis along the cube diagonal. In case of the cubic NaCl structure the trigonal distortion is realized by stretching or compressing along the cube diagonal. The CEF Hamiltonian to describe such the distortion takes the form:

$$H_d = -2/3 B_4 (O_4^0 - 20\sqrt{2}O_4^3) + B_2 O_2^0 \qquad (2)$$

The obtained eigenfunctions of the lowest spin-orbital triplet, for $B_4 = +21$ K and $\lambda_{s-o} = -480$ K yielding $\lambda_{s-o}/10$Dq$=0.038$, take a form (only $|L_z, S_z\rangle$ components of the full $|L, S, L_z, S_z\rangle$ function are shown):

$\psi_1 = 0.740 |0,+1\rangle -0.522|+3,+1\rangle + 0.418|-3,+1\rangle$
$\psi_0 = 0.744 |0,0\rangle -0.467|+3,0\rangle + 0.467 |-3,0\rangle$
$\psi_{-1} = 0.740 |0,-1\rangle +0.522|-3,+1\rangle - 0.418|+3,+1\rangle$

For these functions $S_z = \pm 0.9945$ and $L_z = \pm 0.297$, what give the total moment of $m_z = \pm 2.2883$ μ_B. The L_z value of 0.297 is close to the first-order spin-orbit correction (Ref. [11], p. 450) of $8 \cdot \lambda_{so}/10$Dq$=8 \cdot 0.038 = 0.30$.

For the trigonal distortion for $B_2^0 > 0$ the triplet splits into lower singlet and higher doublet. For $B_2^0 < 0$ the doublet is lower. For $B_2^0 = +50$ K the splitting of the ground triplet amounts to 12 K.

The magnetic field, external or internal in the case of the magnetically-ordered state, polarizes two states of the doublet, as is shown in Fig. 2. The intersite spin-dependent interactions H_{d-d} cause the (antiferro-)magnetic ordering. They have been considered in the mean-field approximation with the molecular-field coefficient n acting between magnetic moments $m_d = -(L + g_e S)$ μ_B, $g_e = 2.002324$. The value of n in the Hamiltonian [10, 13]

$$H_{d-d} = n \left(-m_d \cdot m_d + \frac{1}{2} \langle m_d^2 \rangle \right) \qquad (3)$$

has been adjusted in order to reproduce the experimentally-observed Neel temperature. The fitted value of n has been found to be -11.55 meV/ μ_B^2 (= -200 T/μ_B). It means that the Ni ion in the magnetically-ordered state experiences the molecular field of 503 T (at 0 K). This field as well as the magnetic moment become smaller with the increasing temperature and vanish above T_N. The calculated value of the magnetic moment at 0 K in the magnetically-ordered state amounts to 2.53 μ_B, Fig. 2. It is built up from the spin moment m_s of 1.99 μ_B (S_z=0.995) and the orbital moment m_o of 0.54 μ_B, Fig. 3. The increase of m_o in comparison to the paramagnetic state, $\pm$ 0.26 μ_B, is caused by the further polarization of the ground-state eigenfunction by the internal molecular magnetic field. The orbital moment is quite substantial being about 20% of the total moment. The calculated by us moment at 300 K amounts to 2.26 μ_B (m_s= 1.78 μ_B, m_o= 0.48 μ_B) nicely reproducing the experimental result of 2.2±0.3 μ_B for the Ni moment at 300 K [16]. It should be noted that this novel moment value is remarkably larger than old results of 1.64-1.70 μ_B, which have been generally up to now used in theoretical calculations [4, 6]. The magnetic X-ray experiment of Ref. [16] has revealed a substantial orbital moment of 0.32 μ_B and the spin moment of 1.90 μ_B at 300 K.

The trigonal distortion is important for the detailed formation of the AF structure and the direction of the magnetic moment but it only slightly influences the spin and orbital momenta values. The trigonal distortion yielding the singlet charge-formed ground state leads to the moment direction lying in the plane perpendicular to the cube diagonal. Exactly such the moment direction is observed in NiO. Actually, the magnetic ordering occurs along the $\langle 11\bar{2} \rangle$ direction within this diagonal perpendicular plane due to a further slight distortion within the (111) plane [3].

The present model allows, apart of the ordered moment and its spin and orbital components, to calculate many physically important properties like temperature dependence of the magnetic susceptibility, temperature dependence of the heat capacity (shown in Fig. 4), the spectroscopic g factor, the fine electronic structure in the energy window below 3 eV with at least 20 localized states, Fig. 1. The spike-like peak in c(T) at T_N is in perfect agreement with experimental data [17] obtained on a single-crystal specimen that yields "very large, very narrow peak of 65 cal/Kmol" [18]. Ref. [18] provides a detailed critical analysis of literature experimental data with the tabulated recommended data, that are shown in Fig. 4. As the best description of the c(T) dependence in the range 0<T<250 K they give the Debye value of θ of 580 K. In Fig. 4 we provide our rough summation of the calculated c_d(T) contribution and
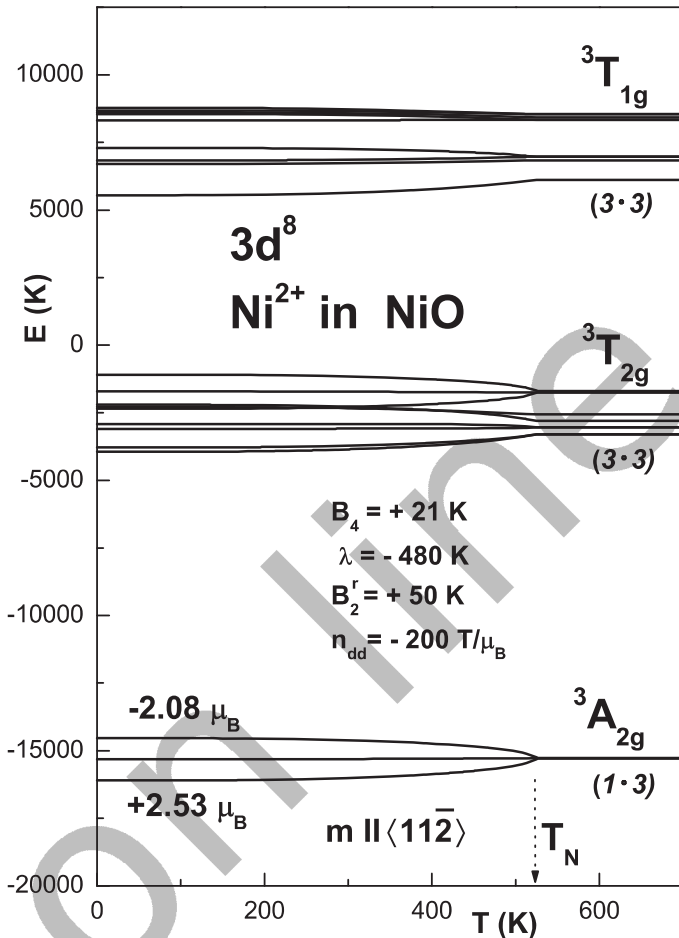
FIG. 2: The calculated temperature dependence of the fine electronic structure of the highly-correlated $3d^8$ electron system in the magnetically-ordered state below T_N of 525 K. In the paramagnetic state the electronic structure is temperature independent unless we do not consider, for instance, a changing of the CEF parameter due to the thermal lattice expansion.

the lattice contribution with a value of θ of 650 K. We find the overall description of c(T) as remarkably good owing too so large temperature interval and the λ-type peak at T_N. The magnetically-ordered state of NiO has lower energy than the paramagnetic one by 3.4 kJ/mol (= 35
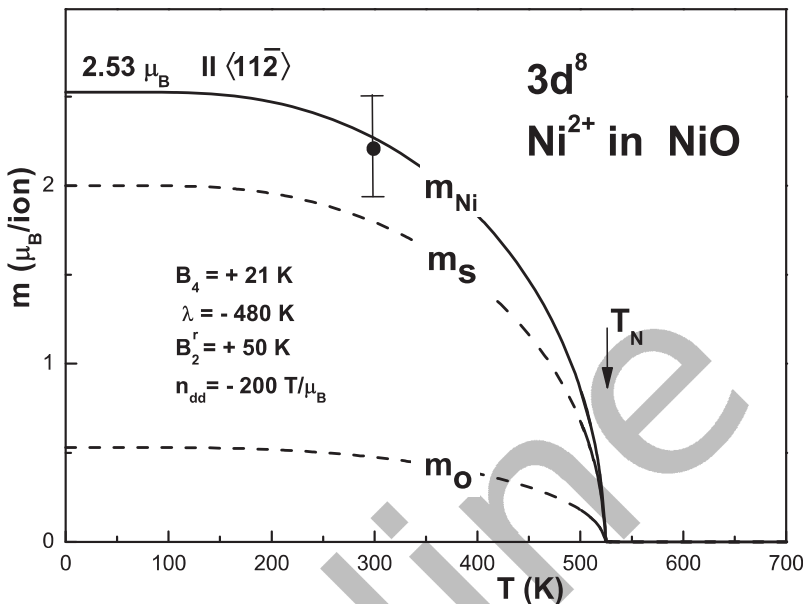
14

FIG. 3: The calculated temperature dependence of the Ni^{2+}-ion moment in NiO. At 0 K the total moment m_{Ni} of 2.53 μ_B is built up from the orbital m_o and spin m_s moment of 0.54 and 1.99 μ_B, respectively.

meV/ion) at 0 K, Fig. 2. Although the molecular field acting on the Ni moment is so large as 503 T it splits CEF states, however, without their reorganization in the lowest triplet. The splitting of the spin-up and spin-down states amounts to 1560 K (135 meV). We think that this energy excitation among the lowest triplet has been revealed by Newman and Chrenko almost 50 years ago [14], who has found a 240 meV excitation. From temperature dependence they have concluded that it is connected with the antiferromagnetic ordering, exactly as comes out from our approach. In our picture this excitation decreases with increasing temperature vanishing at T_N, see Fig. 2.

We would like to point out that our approach should not be considered as the treatment of an isolated ion only - we consider the Ni^{2+} ion in the oxygen octahedron. The physical relevance of our calculations to macroscopic NiO is obvious - the NaCl structure is built up from the face sharing Ni^{2+} octahedra. In the perfect structure all Ni ions experience the same charge (= crystal field) and spin interactions, what means that all Ni ions have the same electronic structure. The good reproduction
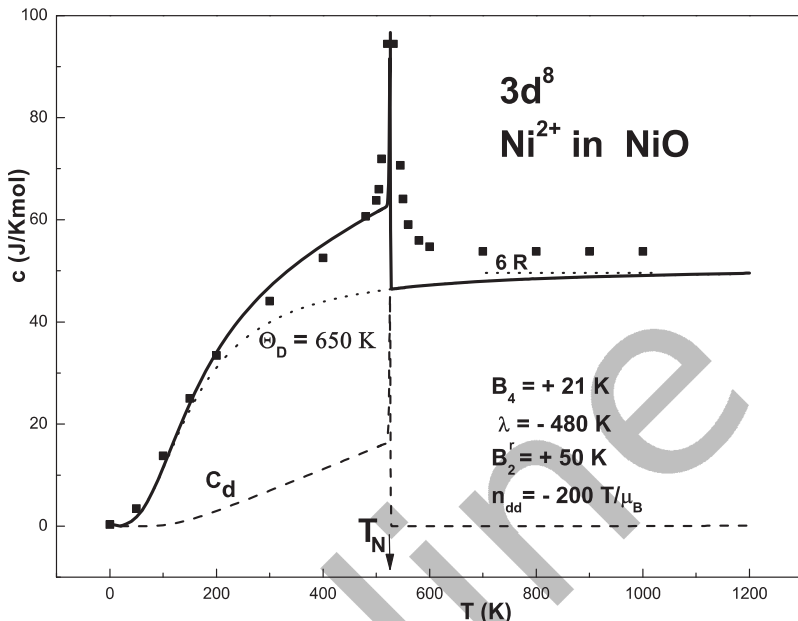
FIG. 4: The calculated temperature dependence of the $3d$ contribution $c_d(T)$ to the heat capacity of NiO. The spike peaks to 214 J/Kmol. A value of 6 R, R is a gas constant, for the high temperature Dulong-Petit heat is shown. Points are the recommended data by Ref. [18] after a critical analysis of literature experimental data.

of macroscopic properties proves that all atoms equally contribute to these properties. But one should remember that due to a finite size of each sample always some atoms on the surface, say 1-2 %, will have another electronic structure like it was discussed in Ref. [9].

In contrary to a general conviction within the magnetic community about the adequateness of the strong crystal-limit to 3d-ion compounds we have found a remarkably good description of NiO in a rather weakly-intermediate CEF limit. The octahedral crystal field is 25 times stronger than the spin-orbit coupling but it does not break intra-atomic correlations among 3d electrons (after giving up two electrons during the formation of a solid NiO, from the 4s states). Such a physical situation is the basis for a developed Quantum Atomistic Solid State Theory (QUASST) for 3d-atom containing compounds [19, 20]. We treat our QUASST approach as a continuation of studies of Van Vleck on cor-

16

relation of macroscopic properties with discrete crystal-field states of transition-metal ions [21].

In conclusion, we have calculated magnetic properties and the electronic structure of NiO both in the paramagnetic and in magnetically-ordered state as well as zero-temperature properties and thermodynamics. We have quantified crystal-field (the leading parameter B_4 = +21 K), spin-orbit (-480 K, i.e. like in the free ion [11]) and magnetic interactions (B_{mol} of 503 T and n= -200 T/μ_B). In our approach $E_{dd} \gg E_{CF}$(=2.0 eV)$\gg E_{s-o}$(=0.29 eV)$\gg E_{mag}$(=0.07 eV). The orbital and spin moment of the Ni^{2+} ion in NiO has been calculated within the quasi-atomic approach. The orbital moment of 0.54 μ_B amounts at 0 K in the magnetically-ordered state, to about 20% of the total moment (2.53 μ_B). Despite of using the full atomic orbital quantum number L=3 and S=1, the calculated effective moment from the temperature dependence of the susceptibility amounts to 3.5-3.8 μ_B, i.e. only 20 % larger value than a spin-only value of 2.83 μ_B. Our success is related to the fact, that we take into account the existence of very strong correlations among electrons. Good description of many physical properties indicates that 3d electrons in NiO are in the extremely strongly-correlated limit, i.e. in the ionic limit confirming *a priori* our atomic-start assumption. In our approach we can trace the Jahn-Teller effect, in the spin-orbital space, and the breaking of the time reversal symmetry, equivalent to the appearance of the ordered magnetic state, at the atomic scale.

We can mention that within the same approach we have described a few 3d compounds like $FeBr_2$ [13], $LaCoO_3$ [22], $Na_2V_3O_7$ [23] and recently CoO [24]. The localized crystal-field states discussed in the present paper are already in a technical use in a ultrafast manipulation of the antiferromagnetism of NiO [25].

♠ dedicated to John Van Vleck and Hans Bethe, pioneers of the crystal-field theory, to the 75th anniversary of the crystal-field theory, and to the Pope John Paul II, a man of freedom in life and in Science.

[1] K. Terakura, A. R. Williams, T. Oguchi, and J. Kubler, Phys. Rev. Lett. **52,** 1830 (1984); A. Gorschluter and H. Merz, Phys. Rev. B **49**, 17293 (1994).

[2] A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984).

[3] M. T. Hutchings and E. J. Samuelsen, Phys. Rev. B **6**, 3447 (1972).

[4] A. B. Shick, A. I. Liechtenstein, and W. E. Pickett, Phys. Rev. B **60**, 10763 (1999); O. Bengone, M. Alouani, P. Blochl, and J. Hugel, Phys. Rev. B **62**, 16392 (2000).

[5] J. I. Igarashi and M. Takahashi, Phys. Rev. B **63**, 184430 (2001).

[6] V. I. Anisimov, F. Aryasetiawan, and A. I. Liechtenstein, J. Phys.: Condens. Matter **9**, 767 (1997); D. I. Khomskii and G. A. Sawatzky, Solid State Commun. **102**, 87 (1997).

[7] I. P. R. Moreira, F. Illas, and R. L. Martin, Phys. Rev. B **65**, 155102 (2002).

[8] S. Hufner, Adv. Phys. **43**, 183 (1994).

[9] R. Gomez-Abal, O. Ney, K. Satitkovitchai, and W. Hubner, Phys. Rev. Lett. **92**, 227402 (2004).

[10] R. J. Radwanski and Z. Ropka, Acta Phys. Pol. A **97**, 963 (2000); arXiv:cond-mat/0005471v1 (2000).

[11] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon Press, Oxford) 1970, ch. 7.

[12] R. J. Radwanski, J. Phys.: Condens. Matter **8**, 10467 (1996).

[13] Z. Ropka, R. Michalski, and R. J. Radwanski, Phys. Rev. B **63**, 172404 (2001).

[14] R. Newman and and R. M. Chrenko, Phys. Rev. **114**, 1507 (1959).

[15] R. J. Radwanski and Z. Ropka, arXiv:cond-mat/9907140v1 (1999).

[16] V. Fernandez, C. Vettier, F. de Bergevin, C. Giles, and W. Neubeck, Phys. Rev. B **57**, 7870 (1998); W. Neubeck, et al., Phys. Rev. B **63**, 134430 (2001).

[17] V. P. Zhuze, O. N. Novruzov, and A. I. Shelykh, Fiz. Tverd. Tela **11**, 1287 (1969); Sov. Phys. Sol. St. **11**, 1044 (1970); after Ref.[18].

[18] J. E. Keem and J. M. Honig, *Selected electrical and thermal data of undoped nickel oxide*, Center for Information and Numerical Data, Cindas Report 52, Purdue University (August 1978).

[19] R. J. Radwanski, R. Michalski, and Z. Ropka, Acta Phys. Pol. B **31**, 3079 (2000);

[20] R. J. Radwanski and Z. Ropka, Acta Physica **2**, 1 (2007), www.actaphysica.eu; arXiv:cond-mat/0010081v1 (2000).

[21] J. H. Van Vleck, Rev. Modern Phys. **50**, 181 (1978).

[22] Z. Ropka and R. J. Radwanski, Phys. Rev. B **67**, 172401 (2003);

[23] R. J. Radwanski and Z. Ropka, Czechoslovak J. Phys. **54**, D427 (2004), arXiv:cond-mat/0309460v1 (2003);

[24] R. J. Radwanski and Z.Ropka, Physica B **345**, 107 (2004), arXiv:cond-mat/0306695v1 (2003).

[25] N. P Duong, T. Satoh, and M. Fiebig, Phys. Rev. Lett. **93**, 117402 (2004).