The atomic-start description of NiO

R. J. Radwanski  
Center of Solid State Physics, S\textsuperscript{th} Filip 5, 31-150 Krakow, Poland,  
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka  
Center of Solid State Physics, S\textsuperscript{th} 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\textsuperscript{2+} ion in NiO. We have obtained that $E_{\text{dd}} \gg E_{\text{CEF}} (=2.0$ eV) $\gg E_{\text{o-o}} (=0.29$ eV) $\gg E_{\text{mag}} (=0.07$ eV). The orbital moment of 0.54 $\mu_B$ amounts at 0 K, in the magnetically-ordered state, to about 20% of the total moment (2.53 $\mu_B$). 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 enormous theoretical and experimental works the consistent description of its properties, reconciling its insulating state with the unfilled 3d shell of the Ni\textsuperscript{2+} ion as a single-ion-like term $H_d$ of the 3d\textsuperscript{8} system and the $H_{d-d}$ intertsite 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 13, 14. For the calculations of electronic states of the quasi-atomic single-ion-like Hamiltonian of the 3d\textsuperscript{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 $\lambda_{\text{o-o}} = -480$ 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 13, 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:

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

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 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\textsuperscript{2+} ion is unstable to lattice 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\textsuperscript{-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
give the total moment of $B^2$ into lower singlet and higher doublet. For
of 0.297 is close to the first-order spin-orbit correction
ground triplet amounts to 12 K. The obtained eigenfunctions of
the full $\lambda d$ orbital moment is quite substantial being about
considered like only 0.5 eV in Ref. 2, 3. For getting
the proper insulating gap an enormous splitting between
spin-up and spin-down $e_g$ states of 10.8 eV was intro-
duced 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 trans-
form 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 compress-
ing along the cube diagonal. The CEF Hamiltonian to
describe such the distortion takes the form:

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

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 $|L_z,S_z|$ components
of the full $|L,S,L_z,S_z \rangle$ function are shown):

$\psi_1 = 0.740 \langle 0,+1 \rangle -0.522 \langle +3,+1 \rangle +0.418 \langle -3,+1 \rangle$

$\psi_0 = 0.744 \langle 0,0 \rangle -0.467 \langle +3,0 \rangle +0.467 \langle -3,0 \rangle$

$\psi_{-1} = 0.740 \langle 0,-1 \rangle +0.522 \langle -3,+1 \rangle -0.418 \langle +3,+1 \rangle$

For these functions $S_z=\pm0.9945$ and $\lambda_{s-o}=\pm0.297$, what
give the total moment of $m_o=\pm2.2883 \mu_B$. The $L_z$ value
of 0.297 is close to the first-order spin-orbit correction
(Ref. 11, p. 450) of 8-$\lambda_{s-o}/10 Dq=8-0.038=0.30$.

For the trigonal distortion for $B_2^2 >0$ the triplet splits
into lower singlet and higher doublet. For $B_2^2 <0$ the
doublet is lower. For $B_2^2 =+50$ 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 coeffi-
cient $n$ acting between magnetic moments $m_d=-(L+g_S)$
$\mu_B$, $g=2.002324$. The value of $n$ in the Hamiltonian

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

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/
$\mu_B^2$ ($=-200$ T/$\mu_B$). 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 tempe-
rature and vanish above $T_N$. The calculated value of
the magnetic moment at 0 K in the magnetically-ordered
state amounts to 2.53 $\mu_B$, Fig. 2. It is built up from the
spin moment $m_s$ of 1.99 $\mu_B$ ($S_z=0.995$) and the orbital
moment $m_o$ of 0.54 $\mu_B$, Fig. 3. The increase of $m_o$
in comparison to the paramagnetic state, ± 0.26 $\mu_B$, is
carried 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 $\mu_B$ ($m_s=1.78 \mu_B$, $m_o=0.48 \mu_B$) nicely reproducing the experimental result of

FIG. 1: The calculated fine electronic structure of the highly-
correlated 3d$^8$ electronic system in the paramagnetic state. a)
the 21-fold degenerated $\Delta F$ 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 octahe-
dral 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 $B^2=\pm50$K. The positive $B^2$
yields the singlet lower - such a situation is favored by the
Jahn-Teller theorem.

FIG. 2: The calculated temperature dependence of the fine
electronic structure of the highly-correlated 3d$^8$ electron sys-
tem in the magnetically-ordered state below $T_N$ of 525 K. In
the paramagnetic state the electronic structure is tempera-
ture independent unless we do not consider, for instance, a
changing of the CEF parameter due to the thermal lattice expansion.

For the description of the trigonal distortion observed
in NiO the cubic Hamiltonian (1) is necessary to trans-
form 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 compress-
ing along the cube diagonal. The CEF Hamiltonian to
describe such the distortion takes the form:

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

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 $|L_z,S_z|$ components
of the full $|L,S,L_z,S_z \rangle$ function are shown):

$\psi_1 = 0.740 \langle 0,+1 \rangle -0.522 \langle +3,+1 \rangle +0.418 \langle -3,+1 \rangle$

$\psi_0 = 0.744 \langle 0,0 \rangle -0.467 \langle +3,0 \rangle +0.467 \langle -3,0 \rangle$

$\psi_{-1} = 0.740 \langle 0,-1 \rangle +0.522 \langle -3,+1 \rangle -0.418 \langle +3,+1 \rangle$

For these functions $S_z=\pm0.9945$ and $\lambda_{s-o}=\pm0.297$, what
give the total moment of $m_o=\pm2.2883 \mu_B$. The $L_z$ value
of 0.297 is close to the first-order spin-orbit correction
(Ref. 11, p. 450) of 8-$\lambda_{s-o}/10 Dq=8-0.038=0.30$.

For the trigonal distortion for $B^2 >0$ the triplet splits
into lower singlet and higher doublet. For $B^2 <0$ the
doublet is lower. For $B^2 =+50$ K the splitting of the
ground triplet amounts to 12 K.
The calculated temperature dependence of the Ni$^{2+}$-ion moment in NiO. At 0 K the total moment $m_N$, of 2.53 $\mu_B$ is built up from the orbital $m_o$ and spin $m_s$ moment of 0.54 and 1.99 $\mu_B$, respectively. The magnetic X-ray experiment of Ref. [16] has revealed a substantial orbital moment of 0.32 $\mu_B$ and the spin moment of 1.90 $\mu_B$ 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 (112) direction within this diagonal perpendicular plane due to a further slight distortion within the (111) plane.

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. Points are the recommended data by Ref. [18] after a critical analysis of literature experimental data.

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 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. [3].

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.
We treat our QUASST approach as a continuation of studies of Van Vleck on correlation of macroscopic properties with discrete crystal-field states of transition-metal ions. In our approach we use a quasi-atomic approach. The orbital moment of 0.54 \( \mu_B \) of the Ni\(^{2+} \) amounts at 0 K in the magnetically-ordered state, to about 20% of the total moment (2.53 \( \mu_B \)). 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 \( \mu_B \) amounts at 0 K in the magnetically-ordered state, to about 20% of the total moment (2.53 \( \mu_B \)). 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 \( \mu_B \), i.e. only 20% larger value than a spin-only value of 2.83 \( \mu_B \). 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 \textit{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\(_3\), LaCoO\(_3\), Na\(_2\)V\(_3\)O\(_7\) and recently CoO. 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.

\* 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. Gorschützer 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); cond-mat/0005471.
[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, cond-mat/9907140.
[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. 22.
[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); cond-mat/0010081.
[20] J. H. Van Vleck, Rev. Modern Phys. 50, 181 (1978).
[21] Z. Ropka and R. J. Radwanski, Phys. Rev. B 67, 172401 (2003); R. J. Radwanski and Z. Ropka, Czechoslovak J. Phys. 54, D427 (2004), cond-mat/0309460.
[22] N. P. Duong, T. Satoh, and M. Fiebig, Phys. Rev. Lett. 93, 117402 (2004).