The low-energy electronic structure
and the orbital magnetism in NiO

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

Z. Ropka
Center of Solid State Physics, 5th Filip 5, 31-150 Krakow, Poland

The orbital and spin moment of the Ni$^{2+}$ ion in NiO has been calculated within the quasi-atomic approach. The orbital moment of 0.46 $\mu_B$ amounts at 0 K, in the magnetically-ordered state, to about 20% of the total moment (2.45 $\mu_B$). For this outcome, being in nice agreement with the recent experimental finding of the orbital moment, taking into account the intra-atomic spin-orbit coupling is indispensable.

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1. Introduction

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 band is still not reached [1, 2, 3, 4, 5].

The aim of this paper is to report the calculations of the magnetic moment of NiO. We attribute this moment to the Ni$^{2+}$ ions. We have calculated the moment of the Ni$^{2+}$ ion, its spin and orbital parts, in the NiO$_6$ octahedral complex and the orbital moment as large as 0.46 $\mu_B$ at 0 K has been revealed. 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 of the Ni$^{2+}$ ions.

2. Theoretical outline

We have treated the 8 outer electrons of the Ni$^{2+}$ ion as forming the highly-correlated 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 $^3F_6$. Such the localized highly-correlated electron system interacts in a solid with the charge and spin surroundings. The charge surrounding has the octahedral symmetry owing to
FIG. 1: The calculated fine electronic structure of the highly-correlated \( 3d^8 \) electronic system. 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, c) the combined action of the spin-orbit coupling and the octahedral crystal field: \( B_4=+2 \) meV, \( \lambda_{s-o}=-41 \) meV.

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 d-d intersite spin-dependent term. Calculations somehow resemble those performed for rare-earth systems, see e.g. Ref. \[7\] and they have been recently applied successfully to 3d compounds \[8, 9\]. For the calculations 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 \( B_4=+2 \) meV - its sign is directly related to the oxygen anion surroundings, the spin-orbit coupling constant \( \lambda_{s-o}=-41 \) meV \[6\], p. 399). The single-ion states under the octahedral crystal field and the spin-orbit coupling have been calculated by consideration of the Hamiltonian:

\[
H_d = B_4(O_4^0 + 5O_4^4) + \lambda_{s-o}L \cdot S
\] (1)
FIG. 2: The calculated temperature dependence of the energy of the three lowest levels showing the splitting of the triplet in the magnetic state (below $T_N=525$ K).

These calculations have revealed the existence of the fine electronic structure, Fig. 1, with the charge-formed states containing three groups of localized states. The higher groups are at 1.2 and 2.1 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 triplet states are characterized by the total moment of 0 and $\pm 2.26 \mu_B$. For the doublet the orbital moment amounts to $\pm 0.27 \mu_B$. It, however, fully cancels in the paramagnetic state and reveals itself only in the presence of the magnetic field, external or internal in the case of the magnetically-ordered state. The magnetic field polarizes two states of the doublet. The intersite spin-dependent interactions cause the (antiferro-)magnetic ordering. They have been considered in the mean-field approximation with the molecular-field coefficient $n$ acting between magnetic moments $m_d=(L+2S) \mu_B$. 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 $-12.2$ meV/ $\mu_B^2$ ($=210$ T/$\mu_B$). It means that the Ni ion in the magnetically-ordered state experiences the molecular field of 518 T (at 0 K).

3. Results and discussion

The calculated value of the magnetic moment at 0 K in the magnetically-ordered state amounts to 2.45 $\mu_B$, 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 0.46 $\mu_B$, Fig. 3. The increase of $m_o$ in comparison to the paramagnetic state, $\pm 0.27 \mu_B$, 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.
FIG. 3: The calculated temperature dependence of the Ni\textsuperscript{2+}-ion moment in NiO. At 0 K the total moment of 2.45 $\mu_B$ is built up from the orbital and spin moment of 0.46 and 1.99 $\mu_B$. The calculations have been performed for the quasi-atomic parameters of the octahedral crystal field $B_4 = +2$ meV, the spin-orbit coupling constant $\lambda_{s-o} = -41$ meV and intersite spin-dependent interactions given by the molecular-field coefficient $n = -12.2$ meV/$\mu_B^2$.

Our theoretical outcome, revealing the substantial orbital moment is in nice agreement with the very recent experimental result of $2.2\pm0.3$ $\mu_B$ for the Ni moment at 300 K [10, 11]. This magnetic x-ray experiment has revealed the orbital moment of $0.32\pm0.05$ $\mu_B$ and the spin moment of $1.90\pm0.20$ $\mu_B$ at 300 K. From the calculated temperature dependence of the total moment, shown in Fig. 3, one sees that the calculated by us moment at 300 K amounts to $2.20$ $\mu_B$ ($m_s = 1.79$ $\mu_B$, $m_o = 0.41$ $\mu_B$) fully reproducing the experimental result. The ground state triplet is further split by the trigonal distortion and/or by the internal molecular field as shown in Fig. 2. Effect of the small trigonal distortion experimentally observed will be discussed elsewhere. It turns out that 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 moments.

We would like to point out that the evaluation of the orbital moment is possible provided the intra-atomic spin-orbit coupling is taken into account. It confirms the importance of the spin-orbit coupling for the description of the 3d-ion compounds despite of relative weakness of the spin-orbit coupling. 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
FIG. 4: The calculated temperature dependence of the $3d$ contribution to the heat capacity of NiO. The spike peaks to 214 J/Kmol. This calculated $c_d(T)$ dependence is in nice agreement with experimental data shown of Refs 12 and 13, where the spike reaches a value of 272 J/Kmol.

20 localized states, Fig. 1. The spike-like peak at $T_N$ is in perfect agreement with experimental data [12] obtained on a single-crystal specimen that yields "very large, very narrow peak of 65 cal/Kmol" [13]. Moreover, we have got that the magnetically-ordered state of NiO has lower energy than the paramagnetic one by 3.4 kJ/mol (= 35 meV/ion) at 0 K. Of course, the energies of magnetic and paramagnetic states become equal at $T_N$.

Finally, 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 edge sharing Ni$^{2+}$ octahedra.

4. Conclusions

The orbital and spin moment of the Ni$^{2+}$ ion in NiO has been calculated within the quasi-atomic approach. The orbital moment of 0.46 $\mu_B$ amounts at 0 K in the magnetically-ordered state, to about 20% of the total moment (2.45 $\mu_B$). For this theoretical outcome, being in nice agreement with the recent experimental finding, taking into account the intra-atomic spin-orbit coupling is indispensable. In our atomic approach we take two Hund’s rules to be valid for description of the ground state of the Ni$^{2+}$ ion - it means that according to our model the Ni atoms preserve their atomic electronic structure also being the full part of a solid. The presented approach explains in a very natural way the insulating state of NiO - in fact, NiO is one of the best insulators. Good description of many physical properties indicates that $3d$ electrons in NiO are in the extremely strongly-correlated limit. In contrary to many considerations yielding a continuous electronic
structure our atomic approach yields the discrete energy states for 3d-electrons in NiO and is in the thinking line of the atomic considerations of Refs. [10] and [11]. As an extra result, these studies have revealed that the Ni$^{2+}$ ion is the Jahn-Teller ion.

A note added 17 December 2004. A very short version of this paper has been published in Acta Phys. Pol. A 97 (2000) 963, only with Fig. 3 [14, 15]. Readers interested in this subject are encouraged to contact us and our papers on "Orbital moment in CoO" [16] and "$^5D$ term origin of the excited triplet in LaCoO$_3$" [17]. Our "Strongly-correlated crystal-field approach to 3d oxides - the orbital magnetism in 3d-ion compounds" one can found as Ref. 18.

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