

Research Article

Orbital moment in NiO

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The orbital and spin moment of the Ni²⁺ 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 more than 20% of the total moment (2.53 μ_B). For this outcome, being in nice agreement with the recent experimental finding, taking into account the spin-orbit coupling is indispensable.

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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 [1–4].

The aim of this short Letter is to report the calculations of the magnetic moment of NiO. We attribute this moment to the Ni²⁺ ions. We

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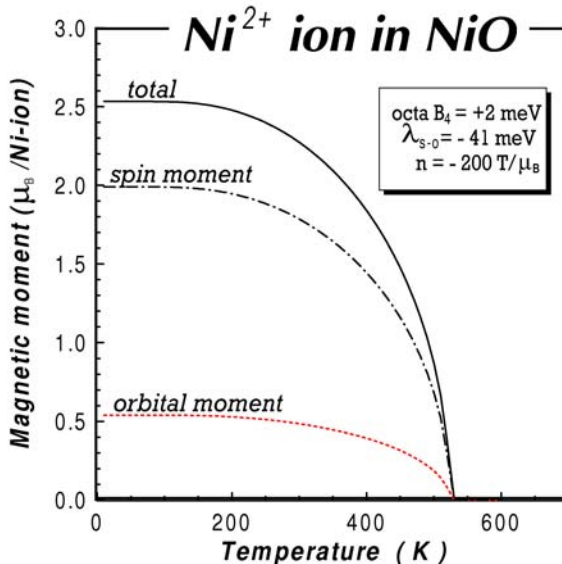


FIG. 1: Temperature dependence of the Ni^{2+} -ion moment in NiO. At 0 K the total moment of $2.53 \mu_B$ is built up from the orbital and spin moment of 0.54 and $1.99 \mu_B$. The calculations have been performed for the quasi-atomic parameters of the octahedral crystal field $B_4 = +2$ meV, the spin-orbit coupling constant $\lambda_{s-o} = -41$ meV and intersite spin-dependent interactions given by the molecular-field coefficient $n = -200$ T / μ_B .

have calculated the moment of the Ni^{2+} ion in the NiO_6 octahedral complex, its spin and orbital parts, and the orbital moment as large as $0.54 \mu_B$ 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 consideration of the atomic-like structure of the constituting atoms/ions, in the present case of the Ni^{2+} ions. 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 [5]. 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 the NaCl-type of structure of NiO. Effect of 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 but it only slightly influences the spin and orbital

moments. 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. [6]. 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 (octahedral CEF parameter $B_4=+2$ meV, the spin-orbit coupling $\lambda=-41$ meV). The single-ion states under the octahedral crystal field and the spin-orbit coupling (the NiO₆ complex) have been calculated by consideration of the Hamiltonian:

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

These calculations have revealed [7] the existence of the fine electronic structure with the charge-formed ground state containing three localized states, originating from the cubic subterm ${}^3A_{2g}$, characterized by the total moment of 0 and $\pm 2.26 \mu_B$. For the doublet the orbital moment amounts to $0.27 \mu_B$. It, however, fully cancels in the paramagnetic state and reveals itself only in the presence of the magnetic field, external or internal in case of the magnetically-ordered state, that polarizes two doublet states. 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 $m=(L+2.0023 \cdot S) \mu_B$. The value of n in the Hamiltonian

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

has been adjusted in order to reproduce the experimentally-observed Neel temperature. The fitted value of n has been found to be $-200T/\mu_B$. It means that the Ni ion in the magnetic state experiences the molecular field of 510 T (at 0 K).

The calculated value of the magnetic moment at 0 K in the magnetically-ordered state amounts to $2.53 \mu_B$. It is built up from the spin moment of $1.99 \mu_B$ ($S=0.995$) and the orbital moment of $0.54 \mu_B$. The increase of m_L in comparison to the paramagnetic state is caused by the further polarization of the ground-state eigenfunction by the magnetic field. The orbital moment is quite substantial being more than 20% of the total moment. Our theoretical outcome, revealing the substantial orbital moment is in nice agreement with the very recent experimental result of $2.2 \pm 0.3 \mu_B$ for the Ni moment at 300 K

[8]. This magnetic x-ray experiment has revealed the orbital moment of $0.32 \pm 0.05 \mu_B$ and the spin moment of $1.90 \pm 0.20 \mu_B$ at 300 K. From the calculated temperature dependence of the total moment, shown in Fig. 1, one sees that the calculated moment at 300 K amounts to $2.2 \mu_B$ fully reproducing the experimental results.

We would like to point out that the evaluation of the orbital moment is possible provided the spin-orbit coupling is taken into account. It confirms the importance of the spin-orbit coupling for the description of the $3d$ -ion compounds [7]. 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, the spectroscopic g factor, the fine electronic structure in the energy window below 3 eV with at least 20 localized states. Our calculations indicate that in NiO at 0 K there is set up the molecular field of 510 T. We have got that the magnetically-ordered state of NiO has lower energy than the paramagnetic one by 3.25 kJ/mol (= 33.5 meV/ion) at 0 K. Of course, these energies are 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 discussion to NiO is obvious - the NaCl structure is built up from the edge sharing Ni^{2+} octahedra.

In conclusion, 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 more than 20% of the total moment ($2.53 \mu_B$). For this theoretical outcome, being in nice agreement with the recent experimental finding, taking into account the intra-atomic spin-orbit coupling is indispensable.

Added during the long and dramatic referee process [22 May 2000]. March 7, 2000 the Editor-in-Chief dr M. Blume has undertook a special discriminating policy with respect to this paper basing on a great number of negative referee reports, of the Editor and of DAE (our proposal for a scientific bet for 1 million dollars). It was despite of our long answers [the whole correspondence is in the following pages], scientific arguments and good agreement with the experiment [8]. (The present paper has been submitted 8.06.1999 but we would like to note that our study of the magnetism and electronic structure of $3d$ -ion compounds started much earlier, about 1995.) The appearance of a paper [9] in Phys. Rev. B in October 1999 clearly proves the importance of our paper. In contrary to Ref. [9] our atomic-like approach provides the

discrete energy states for $3d$ -electrons in NiO [7] and calculates, apart of the spin moment, the orbital moment. This orbital moment is completely ignored in the LDA+U method using the full-potential linearized augmented plane-wave basis of Ref. [9] as well as in many other modern theories [1–4]. The possibility of the calculation of the orbital moment, the moment direction and the thermodynamics of macroscopic properties [10, 11] indicates that our theory cannot be easily rejected. An argument that it is based on the old crystal field theory should be taken rather as a great plus as being well-founded in the solid-state physics.

In a situation of the rejection of this regular article on NiO we were forced to submit a number of Comment - there is an only way to prove to the Editor that the problem of NiO is not solved and is still under present studies. By this we can decline the Editor's claim that my papers on NiO are not suitable and are not of wide interest. Moreover, we can specify the simplifications of just published theories and their inability to reproduce experimental data on magnetism and electronic structure of $3d$ -atom containing compounds. Short after this rejection we submit a Comment to a paper of Schick *et al.* Ref. 9 - PRB BVK716 [12].

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