

**Research Article**

## NiO - from first principles<sup>♣</sup>

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(PRL 19.06.2006, cond-mat/0606604 23 Jun 2006, published 29 December 2006)*

We have calculated from first-principles the octupolar interactions of the Ni<sup>2+</sup> ion in NiO, which gives the theoretical basis for the ionic description of properties of NiO with fully localized strongly-correlated eight *d* electrons. A failure of the up-now first principles ionic calculations for NiO was largely due to too small values taken for the octupolar moment of the transition-metal atom, largely generated by too small value for  $\langle r_d^4 \rangle$ . Our many-electron crystal-field based approach enables successful calculations of the electronic structure and magnetic properties both in the paramagnetic and in magnetically-ordered state as well as zero-temperature properties and thermodynamics.

PACS: 71.10.-w; 75.10.Dg

Keywords: electronic structure, crystal field, spin-orbit coupling, NiO

### I. INTRODUCTION

During last 10 years [1–4] we have described the magnetism and low-energy electronic structure of NiO within the localized atomistic paradigm with only three parameters: the octupolar crystal-field parameter  $B_4 = +21$  K (10Dq=1.086 eV), the spin-orbit coupling  $\lambda_{s-o} = -480$  K and a small trigonal distortion  $B_2^0 = +50$  K [5]. For the magnetic state the fourth parameter, the molecular-field coefficient  $n$ , has been introduced -  $n = -200$  T/ $\mu_B$  yields  $T_N$  of 525 K in agreement

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with the experimental observation. The fundamentally important value of  $B_4$  has been fitted to the excitation of 1.06-1.13 eV seen in the optical absorption [6]. Here we would like to calculate  $B_4$  from first principles - it buckles the internal consistency of our understanding of NiO, explaining its insulating ground state, magnetism both in the AF and paramagnetic state. Although the ionic crystal-field based approach seems to be the most natural approach to transition-atom oxides and is known for 75 years starting with pioneering works of Bethe and Van Vleck [7] the presently in fashion are theoretical approaches pointing out the itinerant (band) character of  $d$  electrons [8–14]. This paper has been motivated by a series of *ab initio* and first-principles papers devoted to explanation of properties of NiO, which recently have been published within the band picture and the continuous energy spectrum [15–20]. We note that with time the original LDA approach is significantly modified by incorporation of different local potentials, i.e. goes towards the advocating by us many-electron crystal-field approach.

## II. THEORETICAL OUTLINE

From historical point of view, the band description has been introduced as an **opposite** view to the ionic view of Van Vleck, which underlies the discrete electronic structure. After works of Van Vleck a milestone achievement within the localized paradigm were the Tanabe-Sugano diagrams known from year of 1954 [21, 22] and shown in Fig. 1 for the  $\text{Ni}^{2+}$  ion. A quite successful description in 1984 by Fujimori and Minami [23] of the photoemission data by a local configuration-interaction cluster model was very soon overflowed by the band-based view pointing out the dominant role played by the covalency and strong hybridization of Ni  $3d$  and O  $2p$  states. In the present situation of the dominant band view in the NiO problem, in general in  $3d$  oxides, we feel necessary to complete our understanding of properties of the magnetism and electronic structure of NiO in the localized paradigm. Our understanding is based on well-known physical concepts like the crystal-field (CEF) [24], spin-orbit (s-o) coupling, local distortions and other terms known from the ionic language. We present this view being aware that the ionic picture and crystal-field considerations are at present treated as the "old-fashioned" and contemptuous physics in times of wide spreading omnipotent band theories of different versions LDA, LSDA, LDA+U [9, 13], LDA+GGA [12], LDA+DMFT [20] and many, many others. We gave a name of QUASST for our approach to a solid containing transition-metal atoms from Quantum Atomistic Solid State Theory

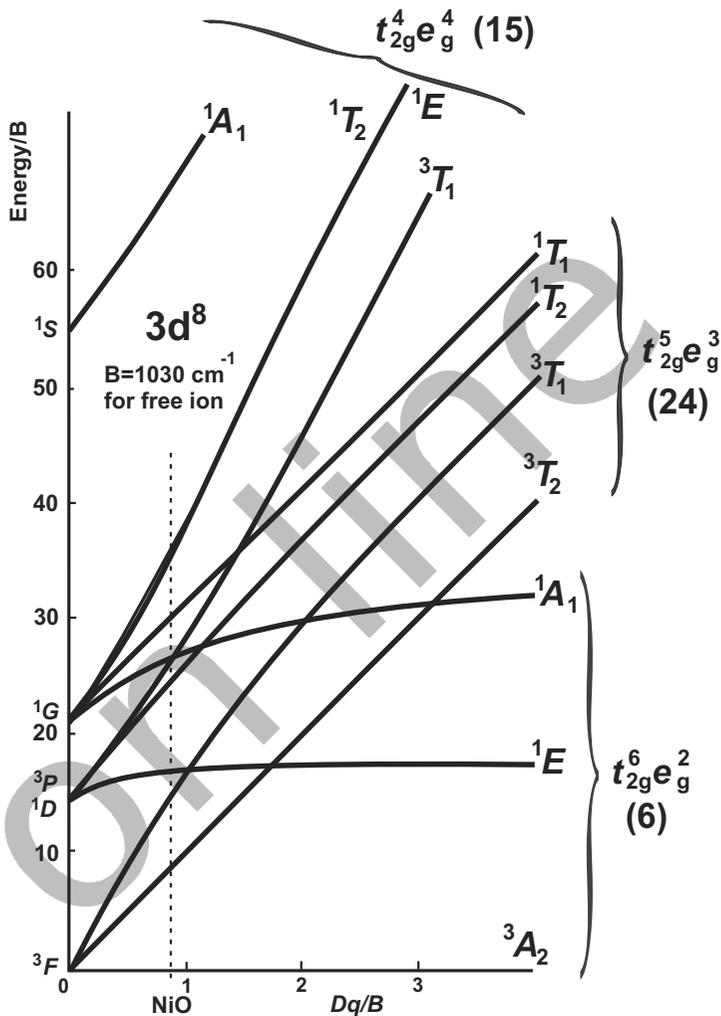


FIG. 1: A Tanabe-Sugano diagram for the  $Ni^{2+}$  ion ( $3d^8$  configuration) showing the effect of the octahedral crystal field on the electronic terms of the free  $Ni^{2+}$ -ion. The electronic structure of cubic subterms, corresponding to  $Dq/B = 0.85$ , relevant to NiO is marked by an arrow. Zero-field term values are presently well known in the NIST database.

pointing out that the physically adequate description of properties of a 3d/4f/5f solid the best is to start from analysis of the electronic structure of constituting atoms. In a solid atoms occur rather as ions by which we understand a well-defined charge state of the given atom.

### III. RESULTS AND DISCUSSION

Schematic steps of the QUASST approach to NiO can be written as:

1. we accept the atomistic structure of matter, what means that atoms preserve much of their atomic properties becoming the full part of a solid. In NiO during the formation of the compound there occurs an electron transfer of two electrons from Ni to O with the simultaneous formation of the rocksalt NaCl lattice with the ionic charge distribution  $\text{Ni}^{2+}\text{O}^{2-}$ ;

2. all magnetism of NiO is related to the  $\text{Ni}^{2+}$  ion with eight electrons outside close configuration  $^{18}\text{Ar}$  because  $\text{O}^{2-}$  ions have closed shells ( $^{10}\text{Ne}$ );

3. eight electrons of the  $\text{Ni}^{2+}$  ion form strongly-correlated atomic-like system,  $3d^8$ ; its electronic structure is known from the atomic physics (NIST [25]:  $^1D - 1.74$  eV,  $^3P - 2.10$ ,  $^1G - 2.86$ ;  $^1S - 6.51$  eV with the  $^3F$  Hund rule ground term);

4. from the translational symmetry of the rocksalt structure of NiO we learn that a) all Ni sites are equivalent, b) the local symmetry of the Ni cation is octahedral, c) the Ni ion is surrounded by six nearest neighbor oxygens forming almost perfect octahedron, d) with the lowering temperature there appears small off-octahedral trigonal distortion;

5. influence of the octahedral crystal field on the free-ion electronic terms as is shown in the Tanabe-Sugano diagram, Fig. 1;

6. influence of the intra-atomic spin-orbit coupling on the local electronic structure; for the free  $\text{Ni}^{2+}$  ion  $\lambda = -42$  meV; NIST [25] gives the multiplet splitting  $^3F - 0.0$  ( $^3F_4$ ), 168.7 meV ( $^3F_3$ ) and 281.4 meV ( $^3F_2$ );
7. influence of the off-octahedral rhombohedral distortion on the local electronic structure;

8. magnetic interactions lead below 525 K to the magnetically-ordered state;

9. having determined the local electronic structure with the eigenfunctions we have the zero-temperature properties as well as the free energy  $F(T)$ ;

10. the zero-temperature properties are related to the properties of the local ground state; the free energy  $F(T)$  enables calculations of the whole thermodynamics. See, for instance, our description of  $\text{FeBr}_2$  [3],

an exemplary of the magnetic  $3d$  compound.

Ad. 1. An assumption about the atomistic construction of matter seems to be obvious but we would like to point out that band-structure calculations for  $3d$  oxides disintegrate  $3d$  atoms completely starting from consideration of all  $3d$  electrons as independent electrons in the octahedral crystal field. According to us these one-electron calculations have to reproduce, before calculations of properties of a solid, the electronic structure of the given ion, i.e. its term structure. For NiO, the  ${}^3A_{2g}$ ,  ${}^1E$  and  ${}^1A_1$  subterm structure of the 6-fold degenerated  $t_{2g}^6 e_g^2$  configuration. In our approach we simply accept the term electronic structure known from the atomic physics (see Ad. 3). We point out that the intraatomic term structure results from strong electron correlations among  $d$  electrons.

Ad. 3. From the atomic physics we know that for the  $3d^8$  configuration of the  $Ni^{2+}$  ion 45 states are grouped in 5 terms:  ${}^3F$  (21 states),  ${}^3P$  (9),  ${}^1G$  (9),  ${}^1D$  (5),  ${}^1S$  (1). The first excited term is almost 2 eV above being inactive for low- and room-temperature properties.

Ad. 4. For more complex structures there will be a few  $3d$  sites, each of them having own electronic structure. Analysis of low-temperature structure is important to decide if all Ni sites are equivalent and all ions equally contribute to macroscopic properties.

Ad. 5. Influence of the octahedral crystal field on the free-ion electronic terms has been calculated by Tanabe and Sugano in a year of 1954 already [21, 22]. The splitting of electronic terms to octahedral subterms in a function of the strength of the octahedral CEF parameter  $Dq/B$  ( $B$  - intra-ionic Racah parameter determines the energy scale) is known as Tanabe-Sugano diagrams, Fig. 1. A problem was and still is with i) the acceptance of its validity for a solid compound and with ii) the evaluation of the value of  $Dq/B$  on this diagram for a given compound. Numerous qualitative indications, starting already at fifties of the XX century, have not been conclusive. In the crystal-field theory parameter  $10Dq$  ( $\cong 600 \cdot B_4$ ) in the simplest form is the multiplication of the octupolar charge moment of the lattice  $A_4$  and of the octupolar charge moment of the involved cation caused by anisotropic charge distribution of the own incomplete  $3d$  shell. Thus  $Dq$  ( $B_4$ ) can be calculated from first principles provided the octupolar charge moment,  $\beta \langle r_d^4 \rangle$ , of the involved ion is known.  $\beta$  is the fourth-order Stevens coefficient.

The octahedral crystal field coefficient  $A_4$  that is the octupolar charge moment of all surrounding charges at the Ni site can be calculated from the point-charge model which is first-principles elementary calculations. Taking the charge of oxygen  $Z$  as  $-2|e|$  and the nearest octahedron with the cation-oxygen distance  $d$  of 208.5 pm in NiO we obtain by for-

mulae  $A_4=7\cdot Ze^2/16\cdot d^5$  [24] a value for  $A_4$  of  $+290 \text{ Ka}_B^{-4}$ ,  $a_B$  is the Bohr radius. Taking for the  $\text{Ni}^{2+}$  ion  $\beta = +2/315$  and a widely-spread Hartree-Fock result by Freeman-Watson (F-W)  $\langle r_d^4 \rangle = 3.003 a_B^4$  [26] a value of  $B_4$  of  $+5.5 \text{ K}$  is obtained only. This value is 3.8 times smaller than the recent experimental determination of  $B_4$  of  $+21 \text{ K}$  [5]. In our papers for  $3d$  oxides ( $\text{LaMnO}_3$ ,  $\text{FeBr}_2$ ,  $\text{CoO}$ , ...) we pointed out that despite this difference the most important is that these ionic *ab initio* calculations give the proper sign of the  $B_4$  parameter - it is important because it determines the ground state of the cation and the experimentally derived strength of crystal-field interactions turns out to be much weaker than it was thought so far in literature for justification of the strong crystal-field approach in which the one-electron approach becomes more physically adequate. Here we would like to explain this theoretical 3.8-times smaller value - we attribute it to a large underestimation of  $\langle r_d^4 \rangle = 3.003 a_B^4$  obtained in F-W Hartree-Fock calculations of in a year of 1965 [26].

At first, we have calculated the contribution to the octupolar lattice potential from next neighbors - it strongly decreases due to the increase of the Ni-O distance. The next-nearest contribution, due to the  $\text{Ni}^{2+}$  ions, amounts to 9% of the first-octahedron contribution but it adds making theoretical evaluation of  $A_4$  as  $+315 \text{ Ka}_B^{-4}$ . Thus, we claim that the proper value of  $\langle r_d^4 \rangle$  for the  $\text{Ni}^{2+}$  ion is  $10.50 a_B^4$  - it is 3.5 times larger value than the F-W Hartree-Fock result from 1965. We claim that this widely-spread early Hartree-Fock result is erroneous. Indeed, the presently derived values are significantly larger. Korotin *et al.* [27] have used a value for  $r_d$  of  $1.26 \text{ \AA}$  yielding approximately  $\langle r_d^4 \rangle = 32.2 a_B^4$ . Recently Solovyev [28], page 5, has calculated for the  $\text{Ti}^{3+}$  ion  $\langle r_d^2 \rangle$  of  $2.27 \text{ \AA}^2$  ( $=8.11 a_B^2$ ), which approximately yields  $\langle r_d^4 \rangle$  even as large as  $65 a_B^4$ . Thus we think that a value of  $10.5 a_B^4$  needed for the purely ionic electrostatic-origin of the crystal-field splitting in NiO is fully reasonable.

Ad. 6. It is fundamentally important to take the spin-orbit coupling into account despite its weakness. Its consequence is that the physically adequate space becomes the spin-orbital space not the orbital space separated from the spin space. It generates, for instance, physically adequate electronic structure of  $d$  electrons and the orbital moment.

Ad. 7. The rhombohedral (trigonal) distortion is small and causes a slight splitting of the lowest quasi-triplet in NiO with  $D$  of order of a few meV (for  $B_2^0$  value of  $+50 \text{ K}$  shown in Fig. 2 D amounts to  $1.0 \text{ meV}$  only). But this small distortion determines in our calculations the direction of the Ni magnetic moment, in NiO the  $\langle 11\bar{2} \rangle$  direction, i.e. perpendicularly to the trigonal axis. Such moment direction causes

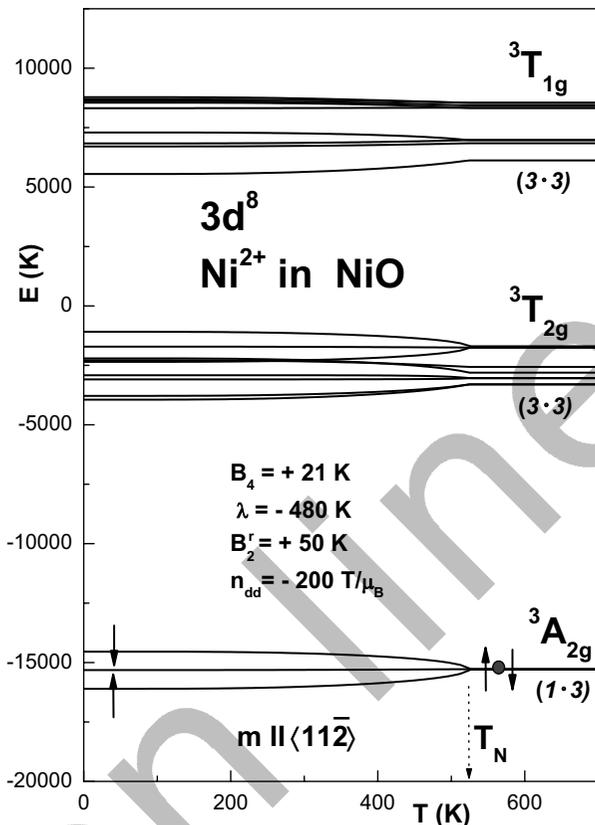


FIG. 2: The calculated temperature dependence of the  ${}^3F$  term ( $Ni^{2+}$ ,  $3d^8$ ) in NiO in the presence of the octahedral crystal field and spin-orbit coupling in the magnetically-ordered state below  $T_N$  of 525 K. In the paramagnetic state the electronic structure is temperature independent unless we do consider, for instance, a changing of the CEF parameter due to the thermal lattice expansion. The states of the  ${}^3A_{2g}$  subterm are characterized by magnetic moment of 0,  $+2.26$  and  $-2.26 \mu_B$ . In the magnetic state there occurs the spin polarization of this three-fold degenerated  ${}^3A_{2g}$  subterm. A small splitting, 1.0 meV, of the  ${}^3A_{2g}$  subterm in the paramagnetic state due to the presence of the trigonal distortion is not visible in this energy scale.

further symmetry lowering due to magnetostriction. Thus, we can say that we fully understand, and we calculate, a delicate interplay of the magnetism of NiO and distortions of its crystal structure.

Ad. 8. The formation of the magnetic state we have described in nu-

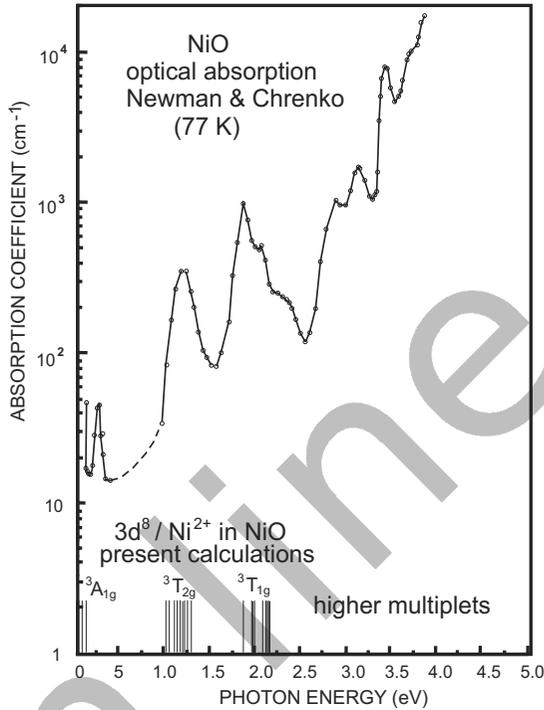


FIG. 3: Comparison of the calculated electronic structure, shown in Fig. 2, with that experimentally observed by means of optical absorption in Ref. [6].

merous compounds - let mention exemplary 4f/3d/5f compounds  $\text{ErNi}_5$ ,  $\text{FeBr}_2$ ,  $\text{NiO}$ ,  $\text{CoO}$ ,  $\text{UPd}_2\text{Al}_3$  and  $\text{UGa}_2$ , results of which have been published starting from 1992. In all these cases the magnetic energy is much smaller than the overall CEF splitting. They are both ionic ( $\text{FeBr}_2$  [3],  $\text{NiO}$ ,  $\text{CoO}$  [2]) and intermetallic ( $\text{ErNi}_5$ ,  $\text{UPd}_2\text{Al}_3$ ,  $\text{UGa}_2$ ) [30] compounds.

We would like to note that all of the used by us parameters (dominant octahedral CEF parameter  $B_4$ , the spin-orbit coupling  $\lambda_{s-o}$ , lattice distortions) have clear physical meaning. The most important assumption is the existence of very strong correlations among 3d electrons preserving the atomistic ionic integrity of the  $\text{Ni}^{2+}$  ion also in the solid  $\text{NiO}$ . We stress the good reproduction of experimental results like temperature dependence of the heat capacity [5], the value of the magnetic moment and its  $\langle 11\bar{2} \rangle$  direction. Our calculations yield a total magnetic moment

of  $2.53 \mu_B$  [5] in very good agreement with recent experimental evaluation [31, 32]. The calculated moment contains almost 20% contribution from the orbital moment. Our purely ionic crystal-field approach, despite its simplicity, is in agreement with recent experimental findings of Jauch and Reehuis [33], who have revealed by the high-accuracy single crystal  $\gamma$ -ray diffraction experiment the electron-density distribution in NiO indicating i) the absence of the covalency and ii) the Ni-O interaction to be purely ionic. For photoemission results we largely accept the Fujimori-Minami interpretation [23] as their cluster result about the multiplet structure, shown in their Fig. 7, is quite similar to our purely ionic multiplet structure, shown in Figs 1 and 3.

#### IV. CONCLUSIONS AND REMARKS

We have calculated from first-principles the octupolar interactions of the  $\text{Ni}^{2+}$  ion in NiO, which gives the theoretical basis for the ionic description of properties of NiO with fully localized strongly-correlated eight  $d$  electrons. The crystal-field interactions are relatively strong in NiO but not so strong to destroy the ionic integrity of the  $3d$  electrons. The insulating gap in NiO of 4.3 eV is of the same origin as a gap in classical insulators, MgO or CaO. A failure of the up-now first principles ionic calculations for NiO were largely due to too small values taken for the octupolar moment of the  $\text{Ni}^{2+}$  ion, largely generated by too small value for  $\langle r_d^4 \rangle$ . Our many-electron crystal-field based approach enables successful calculations of the electronic structure and magnetic properties both in the paramagnetic and in magnetically-ordered state as well as zero-temperature properties and thermodynamics. Thus we claim that this many-electron CEF picture is the physically adequate starting point for description of magnetism and low-energy electronic structure of  $3d$  oxides. Paraphrasing conclusion of Ref. [20] we can say, that in spite of the limitations of the implementation of magnetism and spin-polarization we showed that the ionic CEF-based approach which combines first-principles, material-specific information with very strong electron correlation effects is able to deal with late transition-metal monoxides like NiO. This old-known compound turns out to exhibit subpicosecond switching characteristics of potential applications in spintronics [34, 35].

♣ dedicated to John Van Vleck and Hans Bethe, pioneers of the crystal-field theory, to the 75<sup>th</sup> anniversary of the crystal-field theory,

and to Pope John Paul II, a man of freedom and honesty in life and in Science. Dedicated also to all researchers of NiO - in our understandings we have benefited from all conducting the integral research, both theoretical and experimental.

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