

Research Article

**Comment on Phys. Rev. Lett.'s paper
"All-Electron Self-Consistent GW Approximation:
Application to Si, MnO, and NiO":
band *vs* localized description of NiO**

*R. J. Radwanski**

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

Z. Ropka

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

(Phys. Rev. Lett. 11 December 2006 (LZK 1009); cond-mat/0605567 23 May 2006,
published 28 February 2007)

In contrary to authors of Phys. Rev. Lett. **93**, 126406 (2004) claiming "the band picture to be a reasonable starting point for the description of the electronic structure of NiO, much better than the ligand-field picture", we argue that the many-electron CEF approach is physically adequate starting point for discussion of the electronic structure and magnetism of NiO.

PACS: 75.50.Ee, 75.10.Lp, 71.70.Ej

Keywords: *3d* compounds, orbital magnetic moment, NiO, spin-orbit coupling, crystal field

By this Comment we would like to express our large disagreement about a conclusive statement of a paper [1] in Phys. Rev. Lett. **93**, 126406 (2004) that authors Faleev, van Schilfhaarde, and Kotani "believe that the band picture [23, here Ref. [2]] for NiO is a reasonable starting point for the description of the electronic structure of NiO, much better than previously thought, and in many respects more appropriate than the ligand-field picture." Faleev et al. [1] have performed

* <http://www.css-physics.edu.pl>; Email: sfradwan@cyf-kr.edu.pl

electronic-structure calculations with "a new kind of self-consistent GW (SCGW) approximation based on the all-electron, full potential linear muffin-tin orbital method." getting continuous energy spectrum, a band of d electrons wide by 5-6 eV with a spin-polarization of e_g - e_g states by 2-3 eV similar to that got by Terakura et al. [3, 8]. In contrary to authors of Ref. [1] we argue that the many-electron crystal-field approach, known from works of Bethe and Van Vleck from 1929 with predominantly Ni^{2+} and O^{2-} ions, is physically adequate starting point for discussion of the electronic structure and magnetism of NiO [3, 4, 6]. Being more exact, we claim that the continuous electronic structure for d electrons presented in Figs 2 and 3 of Ref. [1] is not realized in the reality - we claim that in NiO exists the discrete electronic structure.

In our previous Comment [7] to this paper we put attention that the "excellent agreement in the SCGW approach" of the calculated magnetic moment of $1.72 \mu_B$ is based on comparison to too low value derived in 1983 but not to a value of $2.2 \pm 0.3 \mu_B$ at 300 K derived in 1998 [8, 9]. The disagreement becomes larger if one compares a more relevant zero-temperature value of $1.6 \mu_B$.

The description of the electronic structure and magnetism of $3d$ oxides, including famous NiO, is a subject of extensive theoretical and experimental investigations by last 90 years. In recent years the theoretical understanding becomes a subject of enormous controversy when the localized-based view is openly discriminated in Phys. Rev. Lett. and Phys. Rev. B [10]. It is a direct reason for writing of this Comment by us as the publication of Comment is the scientific obligation of each journal considered itself to be scientific. It is obvious that Physics can develop only in the open integral scientific discussion and in the friendly atmosphere, but it is also obvious that in this discrimination takes part great modern physicists acting as referees. This discrimination is the best proof that the most natural and the most elegant approach as the CEF theory is not appreciated in the theory of the solid-state physics at the beginning of the XXI century. Despite it we consequently develop an understanding of transition-metal solids with the discrete electronic structure leaving its solution to the future generation of physicists.

Although the ionic picture is known almost from the beginning of the modern magnetism, in particular from the seminal works of Bethe and Van Vleck on the crystal-field theory and of Tanabe and Sugano on the effect of the octahedral crystal field on $3d$ electronic terms we have extended the single-site CEF theory to the Quantum Atomistic Solid State Theory (QUASST) for $3d$ compounds [11-13] by the correct treatment of the spin-orbit coupling and the recognition that the many-electron CEF approach itself incorporates strong electron correlations

among d electrons already from the beginning. We start analysis of NiO from the detailed analysis of the single-ion effects and the evaluation of the discrete low-energy electronic structure of the Ni^{2+} ion. After the completion with inter-site spin-dependent interactions we have calculated the magnetically-ordered state with the Ni magnetic moment at $T = 0$ K as $2.54 \mu_B$. QUASST allows calculations of the orbital and spin moment as well as physically adequate thermodynamics [4]. The insulating state occurs both in the antiferromagnetic and paramagnetic state. We describe in the consistent way both the paramagnetic and the magnetic state with the description of, for instance, the λ -peak at T_N in the temperature dependence of the heat capacity [13, 14].

QUASST can be practically understood as a demand to start from the very strong electron correlation limit and to evaluate crystal-field interactions the first. It is a surprise that despite long-time studies the basic interactions, like exchange splitting, the ligand-field, the covalency, the hybridization and intra- and inter-sublattice coupling, discussed in the band picture of Refs [1–3], have not been quantified yet. In Ref. [1] they are considered in the eV accuracy. In QUASST we have show that the details of the electronic structure in scale of 1 meV are important. Namely, the trigonal off-octahedral distortion of the 1 meV effect determines the direction of the Ni magnetic moment.

In conclusion, we claim that the ionic-based approach with localized d electrons and with discrete energy states in scale of 1 meV as are discussed in many-electron crystal-field theory is the physically adequate starting point for consideration of the magnetism and electronic structure of NiO. We claim that any approach neglecting very strong correlations among d electrons, the spin-orbit coupling and the orbital magnetism is not physically adequate to $3d$ oxides, in particular not to NiO.

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Added 20.02.2007. This Comment has been written in an abnormal situation in the Phys. Rev. Lett. Office unabling publication of results on the magnetism, electronic structure and the orbital magnetism within the classical many-electron crystal-field approach on NiO and other *3d* oxides whereas papers within other theories, even without any relevance to experimental observations are often published. We challenge referees of Phys. Rev. Lett. being in full respect to them as the best referees - but we also know the scientific importance of our results. The publication of Comment should be the scientific obligation of each journal claiming to be a scientific journal.

ActAPhysica/0702.04 28 Feb 2007