

## Monooxides NiO, CoO and FeO solved!

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We have solved a problem of the magnetism and the insulating ground state of monooxides NiO, CoO and FeO. Our many-electron crystal-field based approach enables successful calculations of the electronic structure and magnetic properties both in the paramagnetic and in the magnetically-ordered state as well as zero-temperature properties and thermodynamics. Our approach is within the strong electron correlations and the strong hybridization limit and the electronic structure is evaluated in the meV scale.

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### I. INTRODUCTION

We have solved an old problem of the magnetism and the insulating ground state of monooxides NiO, CoO and FeO [1, 2]. This problem has been a subject of a fundamental controversy by more than 70 years. Most models basing on the conventional band theory predict FeO, CoO and NiO, having incomplete 3d shell, to be a metal, whereas they are observed to be very good insulators, if stoichiometric. This breakdown of the original band theory of Wilson by 3d oxides was pointed out already in 1937. Despite of 70 years of intense studies the problem of the magnetism and the insulating ground-state of open-shell transition metal (TM) oxides is still under debate. Now we have solved this problem. We have described the insulating ground, the magnetism and

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low-energy electronic structure of NiO, CoO and FeO using the same consistent treatment.

## II. THEORETICAL OUTLINE

We follow our earlier description of FeBr<sub>2</sub> [3] and LaCoO<sub>3</sub> [4]. We have described NiO, CoO and FeO within the localized atomistic paradigm with only three parameters: the octupolar crystal-field parameter ( $B_4$ , 10Dq), the spin-orbit coupling  $\lambda_{s-o}$  and a small off-octahedral distortion  $B_2^0$ . These are the explicit parameters. The most important input parameters are strong electron correlations and strong hybridization. Strong electron correlations cause that most of 3d electrons preserve the atomic-like structure of the divalent ions with  $3d^n$  configuration ( $n = 8$  for NiO, 7 for CoO and 6 for FeO). The intraatomic term electronic structure, known from the atomic physics, results from strong electron correlations among  $d$  electrons. The strong hybridization of 3d/4s electrons of the transition metal and 2p electrons of oxygen causes that 4s electrons transfer to the oxygen fully completing its 2p shell. This effect can be also regarded as the effect of strong intersite electron correlations. The crystal-field interactions are relatively strong in all monoxides but not so strong to destroy the ionic integrity of the 3d electrons. This integrity is underlined in the Quantum Atomistic Solid State Theory (QUASST) which bases on the many-electron crystal-field theory extending to account for the formation of the magnetic state in a transition-metal solid.

The formed crystal-field states are many-electron states of the whole ion but also of the whole crystal. The realized crystal-field splittings seen at the TM sites are an effect of all charge interactions in the crystal. The translational symmetry of the rocksalt structure assures that all TM sites are equivalent. For the magnetic state the fourth parameter, the molecular-field coefficient  $n$ , is introduced. The formation of the magnetic state can be traced in the atomic-scale electronic structure, Fig. 1a.

## III. SOME RESULTS

Calculated phenomena related to the formation of (antiferro-) magnetic state are shown in Fig. 1. Our approach consistently describes zero-temperature properties and thermodynamics. It treats consistently magnetically-ordered state and paramagnetic state with good description of the magnetic phase transition with the  $\lambda$ -type peak at  $c(T)$ , Fig. 1b. Results for experimental observations are collected in Table 1. The many-electron atomistic approach seems to be more physically adequate to monoxides than a single-electron approach being a basis for the band-structure description the discussed.

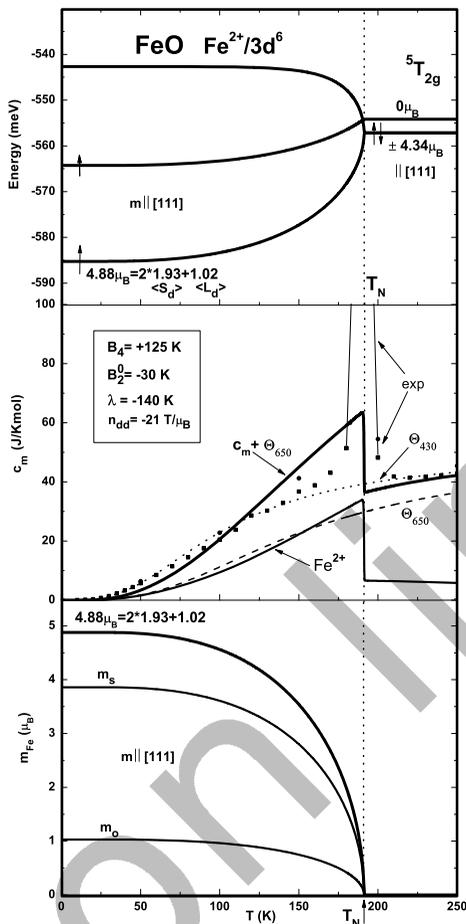


FIG. 1: Calculated phenomena related to the formation of (antiferro-) magnetic state at  $T_N$  of 191 K. top) the splitting of the three lowest states of the  ${}^5T_{2g}$  subterm for the  $Fe^{2+}$  ion ( $3d^6$  configuration) in the octahedral crystal-field in FeO; the moment of the ground state of  $4.88 \mu_B$  is built up from the spin moment of  $3.86 \mu_B$  and the orbital moment of  $1.02 \mu_B$ ; the splitting in the paramagnetic state is due to the trigonal distortion of the octahedral crystal field; middle) Calculated  $Fe^{2+}$  ion contribution to the heat capacity of FeO, the lattice contribution is estimated as being described by the Debye temperature  $\theta_D$  of 650 K; for explanation of the experimental data see Ref. [2]; bottom) temperature dependence of the magnetic moment of the  $Fe^{2+}$  ion in FeO. After Ref. [2].

However, many-electron states can be constructed from single-electron states of the  $3d^1$  configuration in the octahedral crystal field.

The small distortions occurring in all monoxides determine in our calculations the direction of the magnetic moment. Thus, we can say that we fully understand, and we can exactly calculate, a delicate interplay of the magnetism and distortions of their crystal structure. These distortions are manifestation of the Jahn-Teller effect, Fig. 1a.

We would like to note that all of the used by us parameters have clear physical meaning and can be calculated from first principles. In QUASST approach FeO, CoO and NiO are insulators independently on distortions and on the magnetic order, and their a conductivity is

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	Experiment		Our calculations		
	structure distortion	T <sub>N</sub> (K)	T <sub>N</sub> <sup>cal</sup> (K)	m <sub>tot</sub> (μ <sub>B</sub> )	direction
FeO	NaCl	191	191	4.88	diag.
	trigonal				
CoO	NaCl	291	291	4.02	⊥ tetrag.
	tetragonal				
NiO	NaCl	525	525	2.45	⊥ diag.
	trigonal				
	Δ <sub>CF</sub> (eV)	ground subterm	⟨r <sup>4</sup> ⟩ (a <sub>B</sub> <sup>4</sup> )	m <sub>s</sub> (μ <sub>B</sub> )	m <sub>o</sub> (μ <sub>B</sub> )
FeO	1.29	<sup>5</sup> T <sub>2g</sub> (15)	14.8	3.86	1.02
CoO	1.19	<sup>4</sup> T <sub>1g</sub> (12)	12.6	2.99	1.03
NiO	1.08	<sup>3</sup> A <sub>2g</sub> (3)	10.5	1.99	0.46

FIG. 2: Table 1. Experimental data of FeO, CoO and NiO and calculated strength of the octahedral crystal field Δ<sub>CF</sub>, ground term, ⟨r<sub>d</sub><sup>4</sup>⟩, spin and orbital moment at T=0 K.

related to the off-stoichiometry.

#### IV. CONCLUSIONS

We have for the first time consistently described magnetic properties of all three monoxides NiO, CoO, FeO in agreement with their insulating ground state. QUASST reconciles different theoretical approaches underlying coexistence of localized 3d electrons with strong electron correlations and strong 3d-2p hybridization. It turns out that for description of physical properties of NiO, CoO and NiO details of the electronic structure in the meV scale are very important. 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.

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