Specific heat and orbital moment of CoO from first-principles atomistic calculations

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We have for the first time calculated low-energy electronic structure both in paramagnetic and magnetic state as well as zero-temperature properties and thermodynamics. We consistently described magnetic properties of CoO in agreement with its insulating ground state. The orbital moment of 1.42 $\mu_B$ gives 35% contribution to the total moment of 4.04 $\mu_B$ at $T = 0$ K. We have calculated from this low-energy electronic structure the temperature dependence of the specific heat being in nice agreement with experimental data. In our approach CoO is an insulator independently on distortions and the magnetic order.

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I. INTRODUCTION

Understanding CoO and other 3d monooxides is important for the development of the solid-state theory. Their magnetism and the insulating ground state is 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.

Despite of 70 years of intense studies the problem of the magnetism and the insulating ground-state of open-shell transition metal oxides is still under debate [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. We have largely solved this problem working in the purely ionic picture (we call this approach Quantum Atomistic Solid State Theory QUASST). In this paper we present theoretical description of the magnetism and low-energy electronic structure of CoO and the temperature dependence of the specific heat resulting from this structure. We earlier have described NiO [14, 15, 16] and FeO [17] followed by earlier description of FeBr$_2$ [18] and LaCoO$_3$ [19]. In Refs 14-16 we have described 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 $\lambda = - 480$ K and a small trigonal distortion $B_3^0 = +50$ K [14, 15, 16]. These parameters are related to the lowest 21-fold degenerated $^3F$ term. A fourth parameter, the molecular-field coefficient $n_{dd}$ of $-200$ $T/\mu_B$ describes the magnetic state. This $n_{dd}$ value yields $T_N$ of 525 K in good agreement with the experimental observation for NiO.

A direct motivation for this paper is presentation by Kant et al. [20] of new measurements of the specific heat of CoO with an attempt to describe properties of CoO within an ionic model. Also works of Haverkort et al. [21] and Wdowik and Parlinski [22] from the last year contribute to studies of CoO.

II. THEORETICAL OUTLINE AND RESULTS

We have performed detailed calculations of the low-energy electron structure related to the 28-fold degenerated $^3F$ term [23] both in the paramagnetic and magnetic state. We took into account the experimental crystallographic structure - the NaCl-type structure with
scribed for numerous compounds - let mention exemplary splitting of the excited quartets. But this small distortion is related with the octahedral position of the ionic distortion Hamiltonian we take into account the crystal-field interactions (\(n_{d}\)) for the Co\(^{2+}\) ion is 12.6 a\(_{d}\). Calculations have been performed within the same scheme as for FeBr\(_{2}\) \cite{18} and for NiO \cite{19,14,15,16} and other earlier calculations for 4f/5f compounds \cite{24}. In Hamiltonian we take into account the crystal-field interactions (the octahedral crystal field with a small tetragonal distortion \(B_2^{(2)}\)), the spin-orbit interactions  \(\lambda_{\lambda\rightarrow\sigma}\) and inter-site spin-dependent interactions (\(n_{dd}\)). The resulting low-energy electronic structure is shown in Fig. 1. In the magnetically-ordered state there appears a spin-gap of 466 K (=40 meV). The ordered magnetic moment amounts at \(T=0\) K to 4.04 \(\mu_B\) - it is built from the spin moment of 2.62 \(\mu_B\) and the orbital moment of 1.42 \(\mu_B\) \cite{27}. The calculated orbital moment gives 35% contribution to the total moment. The experimentally derived magnetic moment amounts to 4.0 \(\mu_B\) \cite{26}.

The tetragonal distortion is small and causes a slight splitting of the excited quartets. But this small distortion determines in our calculations the direction of the Co magnetic moment, in the CoO case with the c-axis compression, along the tetragonal direction.

The formation of the magnetic state we have described for numerous compounds - let mention exemplary 4f/3d/5f compounds ErNi\(_5\), FeBr\(_2\), NiO, FeO, UPd\(_2\)Al\(_3\) and 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 (FeBr\(_2\) \cite{18}, NiO, FeO \cite{11}) and intermetallic (ErNi\(_5\), UPd\(_2\)Al\(_3\), UGa\(_2\)) \cite{24} compounds. A derived value of \(n_{d}=-43.8\) T/\(\mu_B\) (=29.4 K) in CoO yields the molecular field acting on the Co-ion moment at \(T=0\) K as 176 T - it corresponds to the exchange field acting on the Co spin moment of 271 T and to the exchange energy of 41.2 meV.

The calculated electronic structure very well describes the temperature dependence of the specific heat as is shown in Fig. 2, where the calculated data are compared with experimental data. The calculated temperature dependence of the specific heat of CoO contains three contributions: the 3d contribution \(c_{3d}(T)\) containing both magnetic and Schottky contributions, the lattice and dilution contributions. The magnetic/Schottky contribution is calculated from the derived electronic structure shown in Fig. 1 similarly to that discussed in Ref. \cite{18} for FeBr\(_2\). The dilution contribution is linear with temperature \cite{27} - from thermal expansion and the bulk modulus we calculated its temperature coefficient as 3.4 mJ/K\(^2\) mol (we denote it as \(\gamma_d\) to be distinguished from the electronic Sommerfeld coefficient). The lattice contribution we approximate by the Debye function. We did not have intention to fit perfectly the data but using a value of the Debye temperature \(\theta_D\) of 600 K the experimental data are nicely reproduced in the very wide temperature range, from 0 to 1000 K. Here we give some values. At \(T=200\) K \(c_m=13.27\), \(c_{lat}=33.09\) and \(c_{dil}=0.68\) J/K mol gives total heat of 47.02 J/K mol, which should be compared with 46.03 \(\pm\) (46.63 \(\pm\)) J/K mol. At \(T=400\) K \(c_m=44.78\) and \(c_{dil}=1.36\) J/K mol gives total heat of 53.29 J/K mol, compared to 54.80 J/K mol \cite{27}. At \(T=600\) K \(c_m=54.75\), \(c_{lat}=47.62\) and \(c_{dil}=2.04\) J/K mol gives total heat of 55.01 J/K mol, compared to 54.80 J/K mol \cite{27}. All of these values are very close to experimental data of Refs \cite{20,27} as seen in Fig. 2.

The derived Debye temperature \(\theta_D\) of 600 K is quite similar to a value for \(\theta_D\) of 650 K we have obtained for NiO \cite{15} - it is a very plausible result owing to the structural and compositional similarity of both monoxides.

We would like to note that all of the used by us parameters (dominant octahedral CEF parameter 10\(Dq\) of 1.19 eV (or \(B_2^{(2)}=-23\) K), the spin-orbit coupling \(\lambda_{\lambda\rightarrow\sigma}=-260\) K, lattice distortions \(B_2^{(2)}=-1\) K) have clear physical meaning. The most important assumption is the existence of very strong correlations among 3d electrons what assure the preservation of the atomistic ionic integrity of the Co\(^{2+}\) ion in the solid CoO. We stress the good reproduction of experimental results like temperature dependence of the heat capacity with a \(\lambda\)-type peak, the value of the magnetic moment and, in particular, its direction.

The crystal-field interactions are relatively strong in CoO but not so strong to destroy the ionic integrity of the 3d electrons - it forms conditions for adequacy of the
QUASST theory. The calculated value $10Dq$ of 1.19 eV places CoO at value of 1.0 at the Tanabe-Sugano diagram drawn with $Dq/B$ as abscissa.

III. CONCLUSIONS

We have for the first time calculated low-energy electronic structure both in paramagnetic and magnetic state as well as zero-temperature properties and thermodynamics. We consistently described magnetic properties of CoO in agreement with its insulating ground state. The orbital moment of 1.42 $\mu_B$ gives 35% contribution to the total moment of 4.04 $\mu_B$ at $T = 0$ K. We have calculated from this low-energy electronic structure the temperature dependence of the specific heat being in nice agreement with experimental data. In our approach CoO is an insulator independently on distortions and the magnetic order.

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