Research Article

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Magnetic properties and the electronic structure of LiCoO$_2$♠

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We have described properties of LiCoO$_2$ within the Quantum Atomistic Solid State (QUASST) theory taking into account very strong electron correlations, predominantly of the intra-atomic origin, spin-orbit coupling and the detailed local crystallographic surroundings and its symmetry. Properties of LiCoO$_2$ are consistently explained together with NaCoO$_2$ and LaCoO$_3$ - in all of these compounds the Co^{3+} ions occur in the low-spin state. This low-spin state is the effect of the relatively strong crystal-field interactions ($B_4^z = +320$ K $\iff$ $10Dq = 3.3$ eV) and is a manifestation of the very large orbital moment of the Co^{3+} ion.

I.   INTRODUCTION

Magnetic properties of LiCoO$_2$ are intriguing by at least 30 years. It is an insulator with a wide gap of 2.7 eV and exhibits non-magnetic ground state [1]. Such a non-magnetic ground state is a surprise owing to strong magnetism in metallic elemental Co, a ferromagnet with T_c

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of 1395 K, and an ionic oxide CoO, antiferromagnet with T_N of 292 K. On other side there exists another well-known oxide LaCoO$_3$ which exhibits a non-magnetic ground state. LaCoO$_3$ has been studied by us over last years getting consistent description of its magnetic properties and electronic structure [2] within the Quantum Atomistic Solid State (QUASST) theory [3] taking into account very strong electron correlations and the effect of local surroundings by means of the crystal-field parameters. In similar approach we have described properties of antiferromagnet CoO [4]. A scientific interest to LiCoO$_2$ has recently grown up due to its potential applications in thermopower devices [5] and due to discovery of superconductivity in a sister-compound NaCoO$_2$, when hydrated and off-stoichiometral Na$_x$CoO$_2$ ·yH$_2$O [6, 7]. Theoretical, called "first principles", studies of properties of LiCoO$_2$ within the band picture have been presented in Refs [1, 8] whereas for NaCoO$_2$ in Ref. [9]. An aim of this paper is two fold. At first, we would like to explain magnetic properties of LiCoO$_2$, in particular its nonmagnetic ground state within the localized d-electron picture, following the early works of Van Vleck, and secondly we would like to determine its electronic structure, which can be experimentally verified. It turns out that the physics of magnetic properties and of the electronic structure is much similar to that found in LaCoO$_3$, but with a much deeper-in-energy non-magnetic singlet state and an opposite trigonal distortion.

II.   THEORETICAL OUTLINE

We describe properties of LiCoO$_2$ within the Quantum Atomistic Solid State (QUASST) theory [3, 10, 11], which starts the description of a 3d-4f-5f compound from analysis of the electronic structure of the involved ions. In QUASST we take into account already from the beginning very strong electron correlations, predominantly of the intra-atomic origin, spin-orbit coupling and the detailed local crystallographic surroundings and its symmetry. The insulating ground state of LiCoO$_2$ we understand as resulting from the static ionic charge distribution Li^{1+}Co^{3+}O$_2^{2-}$ established during the formation of the compound. Magnetic properties of LiCoO$_2$ we attribute to the Co^{3+} ions because Li^{1+} and O^{2-} ions are magnetically inactive having closed electron shells. Thus the main point of description of LiCoO$_2$ within the QUASST theory is the very detailed description of the electronic structure of the Co^{3+} ions in the crystallographic structure of LiCoO$_2$. LiCoO$_2$ has a rhombohedral structure, which belongs to the space group R$\bar{3}$m (D_{3d}^5) [1, 9]. The unit cell, with parameters a = 496 pm and $\alpha = 32^o58'$,

contains only one chemical formula unit, and the Co, Li, and O atoms occupy the 1a(0,0,0), 1b(1/2,1/2,1/2) and 2c(x,x,x) with x=0.24, respectively. The rhombohedral structure of $LiCoO_2$ can be viewed as the one derived from the $NaCl$ rocksalt structure of the pure CoO where every second plane of Co atoms stacked in the main diagonal direction is replaced by a plane of Li atoms. Thus, $LiCoO_2$ can be regarded as the layered structure - neutron diffraction results confirm the fully ordered state. For comparison, the rocksalt CoO structure with the conventional lattice parameter $a_c = 426$ pm can be described as the rhombohedral lattice with $a_r = 521.7$ pm and $\alpha = 33^o33^{'}$. The Co atoms in CoO occupy 1a and 1b sites of the $R\bar{3}m$ space group whereas 2c site with x=0.25 (exactly!) is occupied by oxygen atoms. The above presented crystallographic analysis reveals that the cobalt ion in $LiCoO_2$ compound is placed in a local, slightly-distorted, oxygen octahedron. Its diagonal is along the rhombohedral axis. In such structural construction a trigonal distortion can be easily realized by elongation or compression of the distance between the whole oxygen planes. Exactly the same construction of the O-Co-O planes occurs in the perovskite structure, in $LaCoO_3$ [2] for instance, perpendicularly to the cube diagonal, and even in $FeBr_2$ [12], having a hexagonal unit cell. In stoichiometric $LiCoO_2$ there are Co^{3+} ions only. The Co^{3+} ion has six electrons in the incomplete $3d$ shell forming, according to us, a strongly-correlated atomic-like $3d^6$ configuration. It preserves its integrity also in a solid. Such atomic-like system in a crystal experiences the electrostatic crystal field (CEF) due to all surrounded charges. This CEF modifies the term structure in the well-known and fully controlled way, Fig. 1, and substantially removes the degeneracy in the spin-orbital space, Fig. 2.

III. RESULTS AND DISCUSSION

The electronic structure of the Co^{3+} ion is known from the atomic physics and is given in the NIST database [13]. 210 states are grouped in 16 atomic terms. The effect of the octahedral crystal-field has been calculated already 50 years ago by Tanabe and Sugano [14–16]. A modified Tanabe-Sugano diagram for the Co^{3+} ion is shown in Fig. 1. For a relatively weak octahedral CEF, $10Dq < 2.75$ eV, the ground state is a state originating from the high-spin $^5T_{2g}$ cubic subterm - such a situation is realized in $FeBr_2$ and it prefers a magnetic ground state [12]. In $LaCoO_3$ the octahedral CEF is stronger, $10Dq = 2.8$ eV, due to the doubly negative charge of the O ions compared to the single valency of the Br ions and especially due to a small Co-O distance of 193 pm. As a consequence a low-spin $^1A_1$ (^1I) cubic subterm (singlet!!) becomes the ground state [2]. In $LiCoO_2$ the Co-O distance is equally small like in
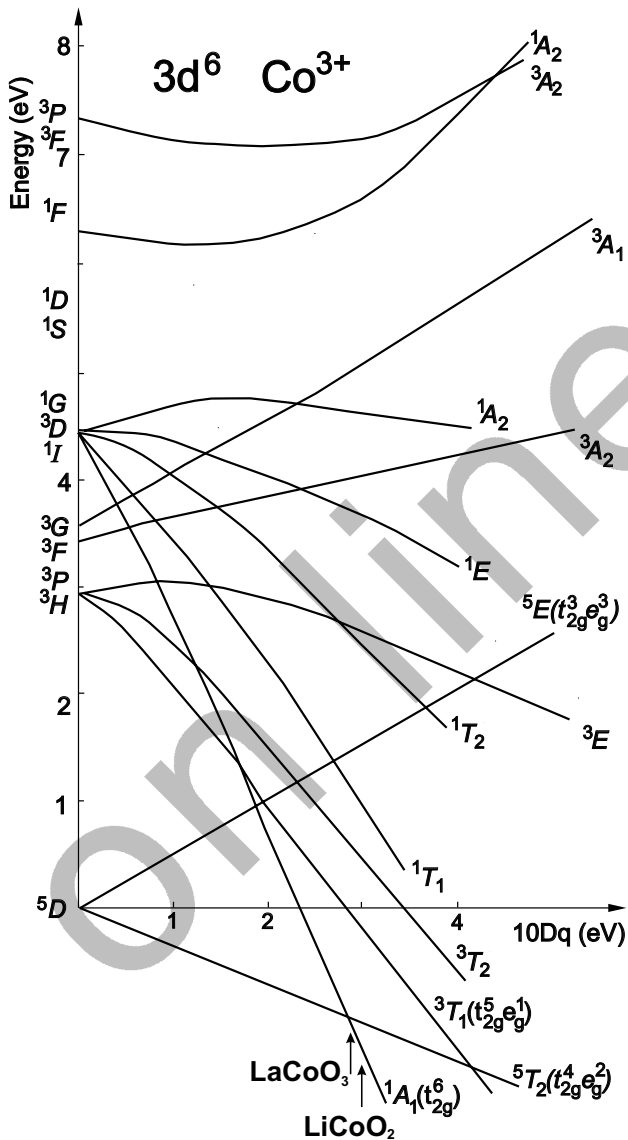
FIG. 1: The modified Tanabe-Sugano diagram for the Co^{3+} ion ($3d^6$ configuration) showing the effect of the octahedral crystal field on the electronic terms of the free Co^{3+} ion. The electronic structure of cubic subterms, corresponding to $10Dq$ of 2.8 and 3.3 eV, relevant to $LaCoO_3$ and $LiCoO_2$ respectively, are marked by arrows.
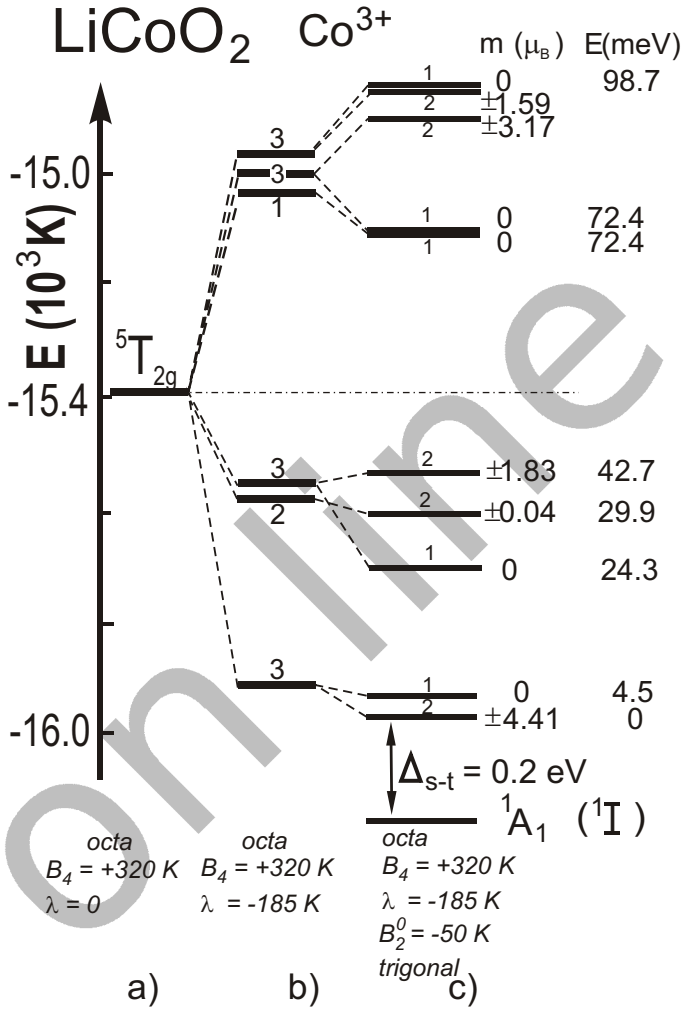
FIG. 2: Calculated low-energy electronic structure of the Co^{3+} ion in $LiCoO_2$ originating from the $^5T_{2g}$ cubic subterm with the $^1A_1$ singlet ground subterm put 0.2 eV below the lowest $^5T_{2g}$ state. Such the structure is produced by the dominant octahedral crystal-field interactions and the intra-atomic spin-orbit coupling (b). c) shows the splitting produced by the trigonal elongation distortion. The states are labeled by the degeneracy, the magnetic moment and the energy with respect to the lowest state of the ^5D term.

LaCoO$_3$ [8] - note that in CoO the Co-O distance amounts to 213 pm, being more than 10% larger. In case $10Dq > 2.75$ eV a non-magnetic state is formed in the atomic scale and such the situation is realized in LiCoO$_2$. 0.2 eV above the $^1A_1$ non-magnetic state there is the lowest state of the high-spin $^5T_{2g}$ cubic subterm (15-fold degeneration) originating from the ionic 25-fold degenerated (in the spin-orbit space) ^5D term. We have calculated its splitting in a trigonal off-octahedral crystal field in the presence of the spin-orbit coupling as is shown in Fig. 2. The used negative sign of B_2^0 corresponds to the trigonal elongation as is experimentally observed. Thus in the ionic model we have got a consistent description of the insulating and non-magnetic ground state. We used only three parameters: octahedral crystal-field parameter $B_4^z = +320$ K $\iff$ $10Dq = 3.3$ eV); the spin-orbit coupling $\lambda = $ -185 K and the trigonal distortion parameter $B_2^0 = $ -50 K. All these three parameters have clear physical meaning and can be calculated really from *first principles* [17, 18]. Of course, the most important assumption is the strong-correlated approach preserving ionic integrity of the $3d^6$ configuration.

We propagate the ionic model. We do not claim, of course, to invent the crystal-field theory, because it was invented in 1929-1932 by Bethe, Van Vleck, Kramers, and many others, but in last 20 years we have provided description of many compounds with the use of the crystal-field theory with the importance of the localized discrete states both in ionic and metallic systems. By this we have proven applicability of the many-electron crystal-field to the solid-state physics [19]. We have extended it from the single-ion theory to the Quantum Atomistic Solid-State theory, QUASST, describing, for instance, consistently both paramagnetic and magnetically-ordered states. We have pointed out for $3d$-ion compounds, for instance, the importance of the spin-orbit coupling [11] and of local distortions. We assume in QUASST, in agreement with experiments, on-site electron correlations to be sufficiently strong to keep the atomic-like integrity of the $3d$ ion in a solid.

We do not know reasons for forgetting or ignoring works on the crystal field of early Van Vleck, Tanabe and Sugano, and of many others. The Tanabe-Sugano diagrams have been almost forgotten in the modern solid state theory [19], likely due to an erroneous conviction that these states are not relevant to a solid material. There is a discussion even on so simple problems as description of the trigonal distortion used by us in Ref. [12] (it is correct) and calculated by us ^5E_g subterm as the ground state of the Mn^{3+} ion in LaMnO$_3$. An argument that the use of the crystal-field to a solid, in particular to metallic magnetic rare-earth systems is erroneous we consider as being not in agreement with exper-
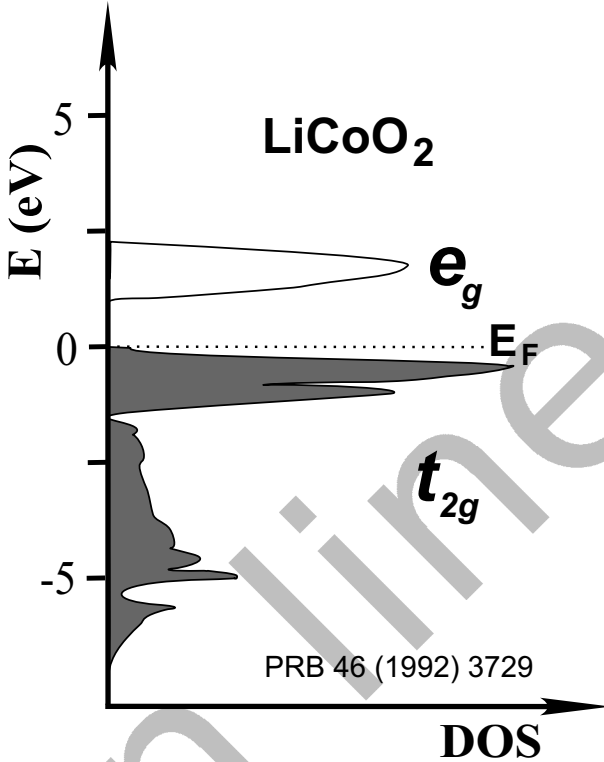
FIG. 3: Schematic electronic structure of d electrons in LiCoO$_2$ obtained within the band theory, after Refs [1] (Fig.4) and [8] (Fig.4a.) According to us this electronic structure is not physically adequate.

imnetal observation. We take as very important the recent revealing in the group of Prof. F. Steglich of localized CEF states in UPd$_2$Al$_3$ and in heavy-fermion metal YbRh$_2$Si$_2$ [20, 21]. After my studies (RJR) with Prof. J. J. M. Franse at the University of Amsterdam on metallic ErNi$_5$, Ho$_2$Co$_{17}$, DyNi$_5$, Nd$_2$Fe$_{14}$B, Pr$_2$Fe$_{14}$B all of these experimental facts prove, according to us, a very substantial usefulness of the crystal-field theory to a solid material, including metallic magnetic rare-earth systems. One of reasons for the limited use of the Tanabe-Sugano diagrams for 3d compounds seems to be caused by the large uncertainty in the strength of the octahedral CEF in a particular compound. From this point of view the exact evaluation of the strength of the octahedral

CEF in $LaCoO_3$ for 2.8 eV [2] we consider to be of the great importance. Note that in the present literature value of $10Dq$ varies in theoretical considerations of $3d$ oxides from 0.5 eV [6], note 32 via 1.3 eV [1] to a poetical saying that it is very strong. QUASST seems to be a standard approach to insulating transition-metal oxides but it has been formulated in times of the ignorance of the crystal field and the overwhelmed itinerant band treatment of $3d$ electrons in the modern solid-state theory. In Fig. 3 we present a band treatment of d electrons in $LiCoO_2$ from Refs [1, 8] which we consider as not physically adequate.

IV. CONCLUSIONS AND REMARKS

We have described properties of $LiCoO_2$ within the Quantum Atomistic Solid State (QUASST) theory. It starts for oxides from the purely ionic charge distribution and takes into account very strong electron correlations, predominantly of the intra-atomic origin, spin-orbit coupling and the detailed local crystallographic surroundings and its symmetry. Properties of $LiCoO_2$ are consistently explained together with $NaCoO_2$ and $LaCoO_3$ - in all of these compounds the Co^{3+} ions occur in the low-spin state (t_{2g}^6, $S = 0$) that is a crystal-field nonmagnetic singlet $^1A_1$. This low-spin state is the effect of the relatively strong crystal-field interactions ($B_4^z = +320$ K $\Longleftrightarrow 10Dq = 3.3$ eV) and is a manifestation of the very large orbital moment of the Co^{3+} ion. The $^1A_1$ state originates from the atomic term ^1I that has $L = 6$. Thanks this large orbital moment the $^1A_1$ subterm becomes in sufficiently strong crystal field the ground state breaking Hund's rules. We consider $LiCoO_2$ as a Mott insulator basing on a definition that the Mott insulator occur due to strong electron correlations despite of the open shell. We claim that the many-electron strongly-correlated CEF approach [10], the basis for QUASST, is physically adequate for $3d$ oxides. The controversy about itinerant-localized treatment of $3d$ electrons between one-electron CEF, many-electron CEF (QUASST) approach and band approaches can be experimentally solved by observation, or not, of the predicted electronic structure. The comparison would be easier if band-structure results contain data verifiable experimentally. At least, effective charges of relevant atoms and experimental predictions for zero-temperature properties and thermodynamics should be reported. The QUASST calculations allow for *ab initio* calculations of magnetic and electronic properties reconciling for $3d$ oxides both insulating, paramagnetic ($LiCoO_2$, $LaCoO_3$, $NaCoO_2$) or magnetic (CoO, NiO, $FeBr_2$) ground state. Note: A paragraph, preceding the last one before the Conclusions, with a discussion of the present scientific situation

within the magnetic community (13.07.2006) has been omitted.

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♠**Dedicated** to Hans Bethe and John H. Van Vleck, pioneers of the crystal-field theory, to the 75th anniversary of the crystal-field theory, and to the Pope John Paul II, a man of the freedom and the honesty in the human life and in Science.

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