Comment on a Phys. Rev. Lett. paper: 94 (2005) 146402: Orbital symmetry and Electron Correlation in Na$_x$CoO$_2$

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We argue that the electronic structure considered in a Phys. Rev. Lett. paper 94 (2005) 146402 of the Co$^{3+}$ ion in the CoO$_6$ octahedron of Na$_x$CoO$_2$ is completely wrong. The presented Fig. 1 is redrawn here as Fig. 1. For physically adequate electronic structure it is necessary to take into account strong intra-atomic electron correlations and spin-orbit coupling. For Co$^{3+}$ ions there are 15 low lying many-electron states within 0.1 eV as can be obtained in the many-electron CEF approach.

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We claim that the electronic structure considered in a Phys. Rev. Lett. paper of Wu et al. [1] for the Co ion in the CoO$_6$ octahedron in Na$_x$CoO$_2$, Fig. 1b, is completely wrong. The presented Fig. 1 in the commented paper is redrawn here as Fig. 1 together with the caption.

An attributing of schematic 5 lines in Fig. 1b to the ionic model we treat as a fun. It is a nonsense, but not an ionic model.

We write this Comment as this nonsense is almost typical for Phys. Rev. journals (not mentioning others). Even if the shown states could have some sense for one d electron these electronic states are totally wrong for the Co ion, with 5 (Co$^{4+}$), 6 (Co$^{3+}$) or 7 (Co$^{2+}$) d electrons, in the CoO$_6$ octahedron as is described in the figure caption.

Despite of such strong critics of the theoretical introduction we like the commented paper, in particular its clear conclusion, that their XAS experiment provides "spectral evidence for strong electron correlations of the layered cobaltates". The existence of strong electron correlations in real 3d-ion compounds is exactly this a physical fact that causes the erroneous of Fig. 1b. The necessity of taking into account strong electron correlations in description of 3d-ion compounds we point out from at least 10 years discussing 3d-ion compounds within the (many-electron) crystal-field (CEF) approach extended to a Quantum Atomistic Solid State Theory (QUASST) [2, 3]. Just the presence in the reality of these strong intra-atomic correlations make the single-electron picture, presented in the commented paper, completely inadequate for the cobalt ion.

Before further discussion we would like to say that advocating for the fundamental importance of the CEF approach in combination with the spin-orbit coupling we are aware that all exotic phenomena existing in 3d-ion compounds, in particular in Na$_x$CoO$_2$ cannot be explained in the purely CEF approach. For explaining our point let concentrate on NaCoO$_2$, i.e. x=1 case. In this case for the good stoichiometry sample we expect to have all Co ions in the trivalent state, noted as the Co$^{3+}$ ion. For x<1 sample some Co ions are forced to be in the tetravalent state and consequently we have a complex mixed system that can show new phenomena (Fermi level, itineracy related to a geometrical charge order/disorder, ...). Thus, let concentrate on perfect NaCoO$_2$ with only Co$^{3+}$ ions.

FIG. 1: (a) Illustration of the trigonal distortion of a CoO$_6$ octahedron. Left panel: undistorted CoO$_6$ octahedron with cubic (O$_h$) symmetry. Right panel: compressed CoO$_6$ octahedron with D$_{3d}$ symmetry. The distorted CoO$_6$ is rotated such that the threefold rotation axis is along the c axis. (b) Crystal-field splitting of Co 3d states in distorted CoO$_6$ according to an ionic model and relative energy positions of 3d bands obtained from LDA calculations. Redrawn from Ref. [1] together with the full caption.

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In an ionic model that we propagate by last years (we do not claim to invent the crystal-field theory, as it was invented in 1929-1932 by Bethe, Kramers, Van Vleck and many others, but in last 20 years we propagate the CEF approach being continuously discriminated scientifically; this discrimination with some inquisition incidents of Phys. Rev. Editors (M. Blume, Wells, ..) and of Polish scientific institutions with a help of Prof. H. Szymczak, J. Sznajd, J. Klamut, A. M. Oles, entitles us to feel at scientific institutions with a help of Prof. H. Szymczak, J. Sznajd, J. Klamut, A. M. Oles, entitles us to feel at

\[ \text{LaCoO}_3 \] whereas in CoO occurs the Co\(^{2+} \) ion with the 3d\(^6 \) configuration. Before describing the really-ionic states of the 3d\(^6 \) system we present electronic states for the 3d\(^5 \) configuration. Fig. 2. Such the 3d\(^5 \) configuration occurs in V\(^{4+} \) ion explained in FeBr\(_2\) or Na\(_2\)V\(_3\)O\(_7\) [9,10,11], for instance, or in the Ti\(^{3+} \) ion in LaTiO\(_3\) or YTiO\(_3\). In all these compounds 3d cation sits inside an oxygen/sulphur octahedron, slightly distorted in the reality. From Fig. 2 one can see that even for the purely octahedral symmetry 6 states in the spin-orbital space (= 3 orbital states in the orbital state) are split in the reality by the always present on-site spin-orbit coupling, Fig. 2(2). The scheme 2(1) is equivalent to Fig. 1b (\(O_h\)) of the commented paper though instead of the orbital notation we mark states by their symmetry showing also the related spin.

According to us this electronic structure is seen in experiments like Electron Spin Resonance (ESR) and is a reason for, for instance, anomalous temperature dependence of the paramagnetic susceptibility (violation of the Curie law) and of the heat capacity at low temperatures. Such the electronic structure of the V\(^{4+} \) ion explains the dramatic reduction, by factor 9, of the effective moment in Na\(_2\)V\(_3\)O\(_7\) observed with decrease...
of temperature from 100 K to 5 K \[12\].

In Fig. 3 we present the electronic structure of the 3d\(^6\) configuration occurring in the Fe\(^{2+}\) ion in a slightly-trigonal distorted bromium octahedron in FeBr\(_2\) \[13\]. The local Fe\(^{2+}\) ion surroundings is exactly as it is shown in Fig. 1a right - in FeBr\(_2\) the shown \(z\) axis is along the hexagonal \(c\) axis. The Co\(^{3+}\) ion is isoelectronic to the Fe\(^{2+}\) ion and have exactly the same states. The structure presented in Fig. 3 shows only the splitting of the two Hund’s rules ground term \(5D\) that is 25-fold degenerated. Fig. 3c shows the electronic structure in case of the purely octahedral CEF in the presence of the always-present spin-orbit coupling. Fig. 3e presents the effect of the stretched trigonal distortion - it has been found to occur in FeBr\(_2\) \[13\], that orders magnetically at \(T_N = 14.2\) K. The doublet-singlet splitting has been found experimentally to amount to 0.0028 eV only \[15\]. The case of Fig. 3d occurs for the trigonally compressed octahedron, i.e. exactly the situation shown in Fig. 1b \((D_{3d})\) of the commented paper. Just our Fig. 3d should be compared with the situation presented in the commented paper for the \(D_{3d}\) symmetry on Fig. 1b. Everybody can see enormous difference between these two electronic structures being a reason for this Comment. Surely instead of 5 orbital states shown in the commented paper there are 25 states (in fact, 210 states!!!). The lowest 15 states, originating from the \(5T_{2g}\) cubic subterm, are of the fundamental importance for thermodynamic properties as they can be thermally populated. In the Co\(^{3+}/Fe^{2+}\) ion there are 15 atomic-like states below 0.1 eV. These states are subsequently populated with the increasing temperature. The scheme shown in Fig. 3d has been observed for LaCoO\(_3\) as the excited subterm (due to the relatively strong octahedral CEF interactions the ground state becomes \(^4\)A\(_1\) originating from \(^1\)I atomic term \(\otimes\)). The experimentally found splitting between the singlet-doublet states, that is the effect of the trigonal distortion, amounts to 7.05 K (=4.9 cm\(^{-1}\) = 0.6 meV = 0.0006 eV) only, \[16\] and references within. It is amazing that so small energy difference between electronic states exists in a solid!!!

For completeness we have to add that 25 states shown in Fig. 3 are only a small part of the full ionic electronic structure of the Co\(^{3+}/Fe^{2+}\) ion, that accounts in total 210 states grouped in 16 atomic terms \(\otimes\) \[17\]. The effect of the octahedral CEF interactions on these 16 terms have been calculated by Tanabe and Sugano already 50 years ago \[15\]. These Tanabe-Sugano diagrams have been somehow forgotten in the modern solid state theory, likely due to an erroneous conviction that these states are not relevant to solid materials. Similarly, many-electron CEF states have been used for interpretation of ESR spectra on diluted systems \[18\], but not to a solid, where a transition-metal cation was the full part of a crystalline lattice. However, we would like to mention that a quite similar picture, though schematic, to calculated by us Fig. 3 has been presented by, for instance, Birgeneau et al. \[17\] in Phys. Rev. B in 1972 - we do not know reasons for forgetting works on the crystal field of early Van Vleck, Tanabe and Sugano, of Birgeneau and of many others. Moreover, we cannot understand reasons for almost rejection of the crystal field from the modern solid state physics. We are somehow grateful to the scientific discrimination of Phys. Rev. Editors (M. Blume, Wells, ..), to Polish scientific institutions, to Prof. Prof. H. Szymczak, J. Sznajd, J. Klamut, A. M. Oles as their negative opinions are the best proof for the shortage of knowledge on the (many-electron) crystal field in the XXI century solid-state theory.

Finally, we would like to mention that an enormous separation energy between \(a_{1g}\) and \(e_g\) states in Fig. 1b, right, found in LDA band-structure calculations of 1.6 eV \[19\] we consider as totally wrong and it will be a subject of another Comment. In the commented paper a value for the trigonal distortion effect of 1 eV, mentioned in Ref. 32 of \[1\], is used - this value is, according to us, at least two orders of magnitude too large. In the approach of the commented paper this trigonal distortion is of the same size as the octahedral splitting (the octahedral CEF parameter \(10Dq\) is taken as 0.5 eV (HS) and 1.5 eV (LS) \[20\] in Ref. 32), what we consider as wrong and being in a sharp conflict with the octahedra construction of the Na\(_x\)CoO\(_2\) lattice. Our value \(B_4 = +200\) K corresponds to \(10Dq = 2.06\) eV \[21\]. Recent data indicate for a value \(10Dq\) of 3.0 eV for LaCoO\(_3\) \[22\].

In conclusion, we claim that the electronic structure considered in a Phys. Rev. Lett. paper of Wu et al. \[1\] for the Co ion in the CoO\(_4\) octahedron in Na\(_x\)CoO\(_2\), Fig. 1b, is completely wrong. For physically adequate electronic structure it is necessary to take into account strong intra-electron correlations and spin-orbit coupling. The role of the lattice distortions is very important but their energies are not of order of 1 eV as LDA band-structure calculations yield, but rather of 0.05 eV as obtained in the many-electron CEF approach. The many-electron CEF model, with strong electron correlations, provides in a very natural way the insulating ground state for 3d oxides. Apart of the ground state it allows for calculations of thermodynamics.

### I. APPENDIX A

Description of the trigonal distortion within the crystal-field theory \[20\]. After our paper Phys. Rev. B 63 (2001) 172404 \[21\].

The 25 levels, originated from the \(5D\) term, and their eigenfunctions have been calculated by the direct diagonalization of the Hamiltonian (1) within the \(|LSL_zS_z\rangle\) base. It takes a form:

$$
H_d = H_{cub} + \lambda LS + B_{0}O_{q}^{2} + \mu_d(L + g_s S)B \quad (1)
$$

The separation of the crystal-electric-field (CEF) Hamiltonian into the cubic and off-cubic part is made for the illustration reason as the cubic crystal field is usually
very predominant. In the crystallographic structure of FeBr$_2$ the Fe ion is surrounded by 6 Br ions. Despite of the hexagonal elementary cell Br ions form the almost octahedral surrounding - it justifies the dominancy of the octahedral crystal field interactions. Moreover, this octahedral surrounding in the hexagonal unit cell can be easily distorted along the local cube diagonal - in the hexagonal unit cell this local cube diagonal lies along the hexagonal $c$ axis. The related distortion can be described as the trigonal distortion of the local octahedron. The cubic CEF Hamiltonian takes, for the $z$ axis along the cube diagonal, the form

$$H_{\text{cub}} = -\frac{2}{3} B_4 \cdot (O^0_4 - 20\sqrt{2}O^4_4)$$  \hspace{1cm}(2)$$

where $O^m_n$ are the Stevens operators. The last term in Eq. (1) allows studies of the influence of the magnetic field $\mathbf{H}$.

For remembering, the octahedral CEF Hamiltonian with the $z$ axis along the cube edge takes a form:

$$H_d = B_4 (O^0_4 + 5O^4_4)$$  \hspace{1cm}(3)$$

\[\dag\] dedicated to Hans Bethe, Kramers 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 freedom and honesty in life and in Science.

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[19] H. Szymczak has blamed us in 2002 that we use too weak CEF interactions - now he can see that at present much smaller values, even of 0.5 eV only, are used in theoretical band calculations of Ref. 1. We do not think that he is brave enough to write a Comment to Phys.Rev. Lett..
[20] Prof. H. Szymczak from the Polish Academy of Sciences, the present long-lasting chairman of the Physical Department of PAS, has claimed that the procedure used by us is incorrect what is an erroneous reproach, see an Abragam-Bleaney text-book, for instance. We mention this problem here because if so great physicist as Prof. H. Szymczak is does not know the CEF description of the trigonal distortion it means that the knowledge about CEF is rather small.