Crystal-field states in NaCoO$_2$ and in wet cobalt superconductors (Na$_x$CoO$_2$)$\spidot$

R. J. Radwanski
Center of Solid State Physics, S$\sp{14}$Filip 5, 31-150 Krakow, Poland,
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka
Center of Solid State Physics, S$\sp{14}$Filip 5, 31-150 Krakow, Poland

We claim that for calculations of the electronic structure of 3d oxides very strong electron correlations have to be taken into account similarly to those assumed in many-electron crystal field approach. For Co$^{3+}$ ions in Na$_2$CoO$_2\cdot$yH$_2$O there are 15 low lying many-electron states within 0.1 eV as can be obtained in the many-electron CEF approach with taking into account the spin-orbit coupling. We claim, that the used by us Hamiltonian for the trigonal distortion is correct.

In Na$_2$CoO$_2$ compounds both Co$^{3+}$ and Co$^{4+}$ ions co-exist. In this paper, for a clarity reason, we confine our consideration to NaCoO$_2$ (x=1), where the Co$^{3+}$ ions only exists and a problem of charge disproportionization or segregation does not occur. NaCoO$_2$ has been sintesized recently and it has been found that the Co$^{3+}$ ions in NaCoO$_2$ are in a non-magnetic state and that there is only single Co site. Thus we think that the origin of this non-magnetic state in NaCoO$_2$ is the same as in LaCoO$_3$, where we took into account strong electron correlations and crystal-field interactions. The high energy, 0-4 eV, electronic structure associated with the splitting of single-ion terms by octahedral crystal field is shown in Fig. 2. Depending on the sodium and water content this non-magnetic state can be changed to the magnetic one similarly to the 3d$^6$ ion in FeBr$_2$ because then the strength of CEF decreases leaving the $^5T_{2g}$ subterm as the ground subterm. The splitting of the $^3T_{2g}$ subterm is shown in Fig. 3.

We propagate the ionic model. We do not claim, however, 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 e.g. Polish scientific institutions with a help of Prof. H. Szymczak, J. Sznajd, J. Klamut, A. M. Oles, entitles us to feel at present ourselves as reinventors of the crystal-field in the solid-state physics, the more that we extend it from the single-ion theory to the Quantum Atomistic Solid-State theory, QUASST, pointing out for 3d-ion compounds, for instance, the importance of the spin-orbit coupling and of local distortions. We assume on-site electron correlations to be sufficiently strong to keep the atomic-like integrity of the 3d ion. QUASST deals consis-
in total 210 states grouped in 16 atomic terms \([8, 9, 10]\). 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. [2] together with the full caption. This electronic structure, calculated without electron correlations, we consider to be very oversimplified [11] - we claim that a proper one for NaCoO\(_2\) is that shown in Fig. 3.

For completeness we have to add that 25 states shown in our papers [3,4] 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 \([8, 9, 10]\).

We do not know reasons for forgetting works on the crystal field of early Van Vleck, Tanabe and Sugano, and of many others. The effect of the octahedral CEF interactions on these 16 terms have been calculated by Tanabe and Sugano already 50 years ago \([8, 9]\). These Tanabe-Sugano diagrams have been somehow forgotten in the modern solid state theory \([2,11]\), likely due to an erroneous conviction that these states are not relevant to solid materials. We are somehow grateful to the scientific discrimination of e.g. Polish scientific institutions, to Prof. Prof. H. Szymczak, J. Sznajd, J. Klamut, A. M. Oles because their negative opinions are the best proof for the shortage of knowledge about the (many-electron) crystal field in the XXI century solid-state theory \([12]\). One of reasons for the limited use of the Tanabe-Sugano diagrams was 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\(_3\) \([2]\) we consider to be of the great importance.

Prof. H. Szymczak \([13]\) has claimed that used by us description of the trigonal distortion within the crystal-field theory is erroneous. His reproach was not corrected by following referees J. Sznajd, K. Wysokinski, J. Klamut and A. M. Oles. Thus we repeat here this description after our paper \([4]\).
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:

$$H_d = H_{cub} + \lambda L \cdot S + B_0^2O_0^2 + \mu_B(L + g_sS) \cdot B$$

(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 hexagonal unit cell of FeBr$_2$ the 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

$$H_{cub} = -\frac{2}{3}B_4 \cdot (O_4^0 - 20\sqrt{2}O_4^2)$$

(2)

where $O_m^n$ are the Stevens operators. The last term in Eq. (1) allows studies of the influence of the magnetic field. For remembering, the octahedral CEF Hamiltonian with the $z$ axis along the cube edge takes a form:

$$H_d = B_4 \cdot (O_4^0 + 5O_4^4)$$

(3)

Before the end we summarize the treatment of NaCoO$_2$ within the Quantum Atomistic Solid-State theory (QUASST). QUASST seems to be a standard approach to insulating transition-metal oxides but due to unknown reasons is highly discriminated in the modern solid-state physics. As reasons for the discrimination an oversimplicity is given as well as very-wide undefined statement that the description of magnetic and electronic properties of NiO, YTiO$_3$, CoO, BaVS$_3$, LaMnO$_3$, LaCoO$_3$ is not suitable for publication being not of the broad interest to the physics community. This argument cannot be treated seriously as all these compounds, starting from NiO are continuously discussed in Phys. Rev. B and Phys. Rev. Lett. with the starting point that their magnetic and insulating properties are not yet understood. In QUASST approach we treat the stoechiometric NaCoO$_2$, with the perfect intrinsic crystallographic structure and the single Co site, as a charge-transfer-insulator. During the formation of the compound there occur electron transfer from Na and Co towards oxygen forming Na$^+$Co$^{3+}$O$_2^{-}$. These charges are localized explaining the insulating ground state. Na$^+$ and O$^{2-}$ ions have closed shells, whereas the Co$^{3+}$ ion has six d electrons. The magnetism and the low-energy electronic structure we attribute to the Co$^{3+}$ ions. According to QUASST, formulated in times of the itinerant treatment of 3d electrons, the six d electrons of the Co$^{3+}$ ion form strongly correlated-electron atomic-like system keeping their atomic-like 3d$^6$ integrity, what means that we expect the intra-atomic correlations and the resulting electron term structure to be preserved. Such atomic-like system in a crystal experiences the electrostatic crystal field due to all surrounded charges. This CEF modifies the term structure in the well-known and controlled way, Fig. 2, and substantially removes the degeneracy, Fig. 3.

Although we mention NaCoO$_2$ as a charge-transfer insulator it is better characterized as a Mott insulator if one takes a definition that the Mott insulator occur due to strong electron correlations that prevent inter-site electron hopping. In our picture the inter-site electron hopping, after the charge-transfer during the formation of the compound, is not allowed in NaCoO$_2$ by intra-atomic correlations which cause that a formation of the 3d$^5$ (Co$^{4+}$) or 3d$^7$ (Co$^{2+}$) configurations is energetically unprofitable. The definition of the Mott insulator could be used in order to point out that a given compound is the insulator despite having the open d or f shell. This definition seems to be in a spirit of the original Mott problem that NiO is the insulator having the open 3d shell, i.e. in order to distinguish Na or Al, for instance, with open 3s and 2p shells that are metals from NiO that is an insulator. Then, the Mott and charge insulators distinguish between insulating NiO and MgO. There could be a problem with the classification of stoechiometric TiO$_2$, for instance, which is an oxide with the transition-metal atom but which in the ideal case with Ti$^{4+}$ ions gave up all 3d electrons taking the close-shell configuration. Thus we propose to use the name of Mott insulator for insulating compounds containing transition-metal atoms, in particular for oxides.

In conclusion, we claim that for calculations of the electronic structure very strong electron correlations have to be taken into account similarly to those assumed in the many-electron CEF approach. We claim, that the used by us Hamiltonian for the trigonal distortion is correct in contrary to the Szymczak’s reproach. We claim that the electronic structure of the Co$^{3+}$ ion in NaCoO$_2$ is much more complex than that considered in Ref. 2 and is close to that obtained for FeBr$_2$ and, in particular, for LaCoO$_3$. The triangular trilayer structural blocks in NaCoO$_2$ [14] are similar to those realized in FeBr$_2$. The one-electron CEF structure shown in Fig. 1 from Ref. 2 is only applicable for one d electron in the trigonally compressed octahedron but not to the Co$^{3+}$ ion which has six d electrons. We claim that the many-electron strongly-correlated CEF approach [15], the basis for QUASST, is physically adequate for 3d oxides. This controversy 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. From this point of view it is interesting to find why LDA calculations provide another ground state, i.e. $e_g^3$ as shown in Fig. 1b right [16, 17], than the single-ion CEF. The comparison would be easier if band-structure results contain data verifiable experimentally. At least, effective charges at relevant atoms and resultant experimental predictions should be reported. The QUASST calculations allow for ab initio calculations of magnetic and electronic properties. We assume atomistic construc-
tion of the matter in a sense, that the transition-metal atom becoming the full part of a solid preserve largely its atomic-like integrity. The potentials used in the crystal-field Hamiltonian have clear physical meaning and can be calculated from first principles, from the point charge model in the simplest version. Despite of the difference in \( a_{1g} \) or \( e_g \) ground state between the single-electron CEF and band theory the basic difference is related to an itinerant treatment of 3d electrons and to the origin of the \( t_{2g} \) splitting. In the band theory the energy splitting is determined by the kinetic energy of electrons in contrary to the crystal-field view that the splitting is due to lattice distortions completed in QUASST with the spin-orbit coupling and the very detailed charge distribution in the whole compound. We note, with pleasure, the changing of the band-theory calculated charge distribution in the whole compound. We mention this problem here because if so using 2.1 eV for 10\( Dq \), assume 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. 2. We suppose that he writes a Comment to Phys. Rev. Lett. that too weak crystal field is erroneously considered in Ref. 2, note 32. In Phys. Rev. Lett. and Phys. Rev. B can be found many such papers.

[13] Prof. H. Szymczak from the Polish Academy of Sciences, the present long-lasting chairman of the Physical Department of PAS, has claimed in an official administrative opinion in November 2001 for the Highest Scientific Council of the Polish Government that the procedure used by us and described in Ref. 2 is incorrect. Prof. Szymczak wrote "Nawiasem mowiac dla Hamiltonianu pola krystalicznego o symetrii oktaedrycznej zapisanego w postaci B\(_4\) (O\(_{4\dagger}\) + 5O\(_4\)) wyraz B\(_2\)O\(_2\) opisuje deformacje tetragonalna a nie trygonalna jak twierdzil dr hab. Ryszard J. Radwanski w swoich publikacjach." what translated means: "Notabene, for a crystal-field Hamiltonian with the octahedral symmetry written in a form B\(_4\) (O\(_{4\dagger}\) + 5O\(_4\)) the term B\(_2\)O\(_2\) describes the tetragonal deformation, but not the trigonal one as dr hab. Ryszard J. Radwanski claims in his publications." This reproach is erroneous and unfounded. Nowhere and never I claimed the supposition ascribed to me by H. Szymczak as one can see, for instance, in Ref. 14, the last acapit of the first page, a paper of mine written in 2000. Szymczak wrote his opinion in November 2001 having this publication as the first position of my publication list. 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. Up to today, despite of my many requests for the withdrawing this reproach, Prof. H. Szymczak did not correct this opinion. In normal scientific conditions such a misunderstanding should be easily solved - by Prof. Szymczak and other Polish professors it becomes a way for the scientific inquisition. Another subject of controversy was related to LaCoO\(_3\) and to the ground state of the Mn\(^{3+}\) ion in LaMnO\(_3\). Our paper with calculated by us the ground subterm \( ^7E_g \), with excited the \( ^7T_{2g} \) states, was rejected at the SCES-02 Conference as being in disagreement with the generally accepted view of the lowest \( t_{2g} \) states and higher \( e_g \) states. We believe that Science, Physics in particular, has to be made in the friendly and well-wishing atmosphere. We can disagree about different theoretical approaches but scientific problems have to be solved in the open scientific discussion.

[14] L. M. Helme, A. T. Boothroyd, R. Coldea, D. Prabhakaran, A. Stunault, G. J. McIntyre, and N. Kernavanois, Phys. Rev. B 73, 054405 (2006); cond-mat/0510360 (2005).

[15] R. J. Radwanski and Z. Ropka, cond-mat/0404713 (2005).

[16] D. J. Singh, Phys. Rev. B 61, 13397 (2000); 68, 020503(R) (2003).

[17] K. -W. Lee, J. Kunes, and W. E. Pickett, Phys. Rev. B 70, 045104 (2004).

[18] W. Koshiba and S. Maekawa, Phys. Rev. Lett. 91, 257003 (2003).

URL: http://www.css-physics.edu.pl dress: sfradwan@cyf-kr.edu.pl