History - 1999

Preservation of the individuality of 3d atoms in a solid

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(under law and scientific protection of Phys. Rev. Lett. LL7701 from 30 June 1999 and of Phys. Rev. B from 9 June 2001; arXiv:cond-mat/0006092v1, 6 June 2000; related to: Acta Physica **2** (2007) 1; published 31 December 2008; online: www.actaphysica.eu)

On basis of analysis of experimental results for more than 200 compounds with 3d and 4f elements we conjecture that atoms with unfilled 3d and 4f shells preserve much of their atomic properties, manifested by the discrete electronic structure, even then when they become the part of a solid. As a consequence, electronic and magnetic properties of the 3d-ion containing compounds are strongly affected by the existence of the atomic-like crystal-field fine electronic structure.

PACS: 71.10.-w; 75.10.Dg
Keywords: 3d compounds, strongly-correlated electron systems, crystal field

The discovery of the high-temperature superconductivity in the copper oxides has revealed the enormous shortage of our general understanding of the 3d-ion compounds. For example, the insulating state of La_2CuO_4 contradicts the standard band-structure result that predicts it to be metal [1, 2]. This dramatic breakdown of the ordinary band-structure theory has been known already for years for 3d-ion monooxides and it was Sir N. F. Mott who has realized it already 50 years ago (due to him the insulating 3d compounds are presently known as Mott insulators). His problem why NiO, for instance, having unfilled 3d shell is insulator is still not clear. Different reparations of the conventional band-structure theory, which treats d-electron states to form the continuum energy band do not lead to the consistent picture for 3d-ion systems. On basis on analysis of more than 100 compounds containing 3d elements we strongly believe that the incorrect treatment of the 3d atom is the reason for it. By this Letter we put a conjecture that 3d elements even then when they become the part of a solid preserve much of their atomic properties similarily to the understanding of the 4f rare-earth systems.

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By atomic properties we understand the existence of the discrete energy spectrum (with the energy separation even below 1 meV) and by this conjecture we say that this discrete atomic-like electronic structure is preserved when the $3d$ atom becomes the part of a solid. This discrete electronic structure is superimposed on the electronic structure of the whole compound. This atomic-like structure predominantly determines the electronic, magnetic and transport properties as well as their temperature dependence. The explanation of electronic, magnetic and transport properties of solids is the main goal of the solid-state physics. The possibility of calculations of the temperature dependence of macroscopic physical properties of a solid is the great advantage of the present atomic-based model as it is possible for $4f$ systems.

Coming to details, our conjecture means that n d electrons in the unfilled $3d$ shell form, like in the atom, a highly-correlated electron system $3d^n$ by means of intra-atomic interactions. This object, having own spin and orbital momentum, interacts with the surrounding charge and spin. As an example, let consider $LaCoO_3$. In accordance with its insulating state we have ionic configurations: $La^{3+}Co^{3+}O_3^{2-}$. The La^{3+} and O^{2-} ions are largely inactive in the electronic and magnetic properties having the full Xe-like and Ne-like configuration though they are taking important role in the bonding (via conventional electrostatic interactions, also multipolar) and the formation of the solid due to the electronic charges. Then we have to consider the discrete energy spectrum of the Co^{3+} ion ($3d^6$ electronic system) that by intra-atomic interactions takes the term ^5D as the ground term (two Hund's rules). This ground term being 25-fold degenerated is split by (multipolar) electrostatic interactions (Stark-like effect) and in case of magnetically-ordered systems, not the case of $LaCoO_3$, by Zeeman-like effect. Of course, for the detailed discussion we need to know the exact charge and spin distribution (the main goal of local-density approximation theories). It is still the unsolved problem in the solid-state physics. There is, however, a solution of this tremendous problem. We can learn a lot about the splitting and the ground state already from the local symmetry of the multipole electrostatic interactions (the crystal electrostatic field) with the use of the group theory. In refs [3] and [4] we have shown that in the case of the perovskite-like structure relevant to $LaCoO_3$ the ground state of the Co^{3+} ion in the slightly-distorted octahedral symmetry is a nonmagnetic singlet. This atomic-like explanation of the 50-years lasting problem of the low-temperature diamagnetism and its temperature transformation to the paramagnetic state deserves on the special attention due to its physical simplicity and the good foundation within physical concepts. Moreover, this our solution leads to the substantial unification of atomic

and solid-state physics.

The scientific intriguity of $LaCoO_3$ is related with the experimental fact of the drastic violation of the theoretical S=2 temperature dependence of the paramagnetic susceptibility at low temperatures, i.e. with the violation of the Curie-Weiss law. According to us this drastic violation of the Curie-Weiss law is related with the existence of the discrete energy states. In case of $LaCoO_3$ there are 15 discrete states [3, 4] within 300 meV. It yields the average energy separation of 20 meV. Obviously, the existence of such atomic-like fine electronic structure affects enormously electronic and magnetic properties of the whole compound. For the Mn^{3+} ion in the octahedral nearest-neighbour oxygen surrounding 10 states of the ${}^5E_g$ subterm are contained within 10 meV [4]. The extremally small energy separation occurs for the $3d^n$ systems with the odd number of d electrons. For these systems the Kramers doublet is the charge-formed ground state. This Kramers degeneracy is later spontaneously removed by interactions involving the spin, i.e. with the breaking of the time-reversal symmetry and the formation of the magnetic state.

We can ask: "Is this atomic idea a new one in the solid-state physics?" Yes and no. No, as most of experimentalists naturally discuss their results in terms of local properties. Yes, as according to our knowledge noone has been able to resist to presently-in-fashion solid-state physics theories that simply ignore the existence of the atom in the solid arguing that the solid is so many-body object and that there are so strong intersite correlations that the individuality of atoms is lost. In the standard band-structure calculations the d electrons are taken as itinerant forming a band of about 5 eV width. In the band there is a continuum of the energy states within 5 eV. In our model there are discrete states with energy separations more than 1000 times smaller. No, as there are some text books written about the crystal field, let mention a book of Abragam and Bleaney [5] or Ballhausen [6]. Yes, as they applied the CEF approach to some diluted systems, not to the concentrated ones. Yes, as they have not been consequent enough and by discussing different crystal-field approaches (weak, strong, ...) with further concepts they largely washed up the original idea. Please note that in the strong CEF approach the n $3d$ electrons are treated as largely independent, i.e. they do not form the highly-correlated $3d^n$ system in contrary to the present model. Our approach corresponds to the intermediate crystal-field approach, but we point out the fundamental importance of the intra-atomic spin-orbit coupling, despite of its relative weakness for the $3d$ ions [7]. Also yes, as at present this atomic-like picture is enormously prohibited in the leading physical journals and a little is said about the

discrete states in the magnetic and strongly-correlated electron system conferences. We understood our approach as the continuation of (some) ideas of Bethe, Kramers, Van Vleck, Mott, Anderson, Hubbard, ...who pointed out the importance of local-scale effects on magnetic and electronic properties.

The existence of these discrete states, with the energy separation below 1 meV has been already well evidenced for conventional rare-earth systems ($4f$ shell) though strong discussion is going on about their existence in anomalous rare-earth systems, namely with Ce and Yb. The good description of electronic and magnetic properties of intermetallics $ErNi_5$ [8] and $NdNi_5$ [9] indicates on the substantial preservation of the individuality of the Er^{3+} and Ni^{3+} ions also in intermetallic compounds. For description of the intermetallics the atomic-like approach has been extended to the individualized-electron model that considers the coexistence of ($4f^n$)localized- and itinerant-electron subsystems. Here we should mention a surprisingly good description within the individualized-electron model of magnetic and electronic properties of the actinide intermetallics UPd_2Al_3, UGa_2 and $NpGa_2$ [10, 11] as originating from the discrete states of the U^{3+}/Np^{3+} ions. Macroscopic properties can be obtained at the quantitative level from the microscopic ones by the direct multiplification by the number of the transition-metal ions involved (to be specific, the molar heat capacity value, for example, is obtained from the atomic value via Avogadro number). It is worth noting that our approach reveals very strong correlation between the local magnetism, the local crystallographic symmetry (Jahn-Teller effect) and the fine electronic structure.

We would like to add, preceding unfounded critics, that we do not claim that everything can be explained only by single atoms but our point is that the proper, i.e. physically adequate starting point for the discussion of properties of a solid containing the open shell elements is the consideration of its atomic states. Our numerous computer experiments point out that e.g. the orbital moment has to be "unquenched" in the solid-state physics of $3d$-ion containing compounds and our approach enables it. For instance, we have derived the orbital moment in NiO to be 0.54 μ_B what amounts to 20 % of the total moment (2.53 μ_B) [12]. Moreover, one should not consider our approach as the treatment of an isolated atom - we clearly discuss the cation octahedra. The whole NaCl structure of NiO is built up from the edge sharing cation octahedra. The perovskite structure, for instance, is built up from the corner (and the edge) sharing cation octahedra along the c direction (in the a-b plane).

In conclusion, on basis of the extended analysis of experimental re-

sults for the great number of compounds (more than 200, including $4f$ and $5f$ compounds) we put a conjecture that in compounds containing atoms with unfilled $3d$ /$4f$ /$5f$ shells there exists the discrete electronic structure associated with quasi-atomic states of the involved ions. The existence of such the structure causes dramatic changes of the low-temperature electronic and magnetic properties like the formation (or not) of the local magnetic moment and its long-range magnetic order, temperature dependence of the magnetic suceptibility and of the heat capacity [3, 8–11].

For the better illustration of our point of view the reader is asked to look into recent Phys. Rev. Lett.' papers. In Ref. [13] authors, considering states of two $3d$ electrons of the V^{3+} ion in V_2O_3, came out with the continuum electronic structure spread over 2.5 eV (Figs 2 and 3). In Fig. 8 of Ref. [14] the continuum electronic structure for six $3d$ electrons in FeO spreads over 8 eV. By this Letter we put the conjecture that in both cases there are crystal-field discrete energy states as have been discussed in Refs [3] and [4] following the original idea of Bethe from 1929. In FeO, in the paramagnetic state, quite similar structure to that presented in Refs [3] and [4] is realized. Our approach is in agreement with the general conviction about the importance of the electron correlations in description of open-shell compounds - in our approach we start from the very strongly-correlated limit in contrary to a weak correlation limit of the LSDA approach. We are convinced that the publishing of our paper enables the open scientific discussion on the magnetism and the electronic structure of $3d$ /$4f$ /$5f$-atom containing compounds and we are ready for this discussion.

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Added 30 Dec 2008: after our submission 6 June 2001 to arXiv, 8 June 2001 we have got email from V. Yu. Irkhin and Yu. P. Irkhin:

Dear Prof. Radwanski,

We have read with great interest the preprint of your paper "The preservation of the individuality of $3d$ atoms in a solid".

We work on similar questions.

In particular, we bring your attention to our unpublished book "Electronic structure, correlation effects and physical properties of d- and f-metals and their compounds" (cond-mat/9812072) and the review paper "Many-electron operator approach in the solid state theory" Phys. Stat. Sol. (b), 1999, v. 193, N1, p. 9-58.

Yours sincerely

V. Yu. Irkhin and Yu. P. Irkhin

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