

Quantum Atomistic Solid-State Theory: CeRh_2Si_2 , K_2CoF_4 , LaCoO_3 , Sr_2VO_4 , Ba_2IrO_4 and Sr_2RuO_4

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The propagated crystal-field-based quantum atomistic solid-state theory starts the theoretical description of a solid containing open d/f shell atoms from the analysis of charge states and low-energy crystal-field discrete electronic structure of $3d/4f/5f/4d/5d$ ions. The crystal-field-based description of CeRh_2Si_2 Kondo-lattice antiferromagnetic intermetallics proves that crystal-field states exist in the compounds’ “conducting current”. In oxides, the realized cation valency is basically equal to the formal valency from the ionic model. The realized valency can be experimentally verified by having its own finger print in the excitation spectrum. Even weak spin-orbit interactions in $3d$ ions are responsible for the violation of the Curie-Weiss law at low temperatures, and for the realization of the nonmagnetic state, especially for non-Kramers ions, as it is in the case of Sr_2RuO_4 . The quantum atomistic solid-state theory methodology “From atomic physics to solid-state physics” is very fruitful and offers a consistent picture of transition-metal compounds.

topics: crystal-field (CEF), spin-orbit interactions, oxides

1. Introduction

Long studies are underway in order to find a common basis for a consistent theoretical understanding of the properties of compounds containing transition-metal atoms with open $3d$ and $4f/5f$ shells. Since about 10 years ago, iridates and ruthenates have become intensively studied having open $5d$ and $4d$ shells [1]. Surely such a scientific project is a very ambitious one, involving about 2/3 of the Mendeleiev table. One can see from the above definition that we use the name “transition-metal” (TM) atoms for all $3d/4d/5d/4f/5f$ atoms not only for $3d$ ones — such an extension is more and more often used in the current literature.

Within the TM compounds, one meets many different compounds as intermetallics and insulators. Within intermetallic compounds, there are compounds exhibiting heavy-fermion (h-f) and Kondo-lattice phenomena that are strongly different from conventional rare-earth compounds. Within insulators, one meets Mott or charge/band insulators exhibiting, for instance, metal-insulator transitions and complex magnetic properties. Among them, special interest take the oxides, which violate somehow the Wilson band theory, being insulators despite the incomplete $3d$ band as in typical monoxides CoO , NiO or FeO .

Developed and propagated by the present author, the quantum atomistic solid-state theory (QUASST) [2–5] starts the theoretical description

of a solid containing open d/f shell atoms from the analysis of the charge distribution within the elementary cell and the analysis of the low-energy, below say 25 meV (equivalence of thermal room-temperature energy), the electronic structure of the involved $3d/4f/5f/4d/5d$ ions, placed in the crystal, with respect to the observed magnetic properties [6, 7]. The title of one of our paper from 2000 “From atomic physics to solid-state physics: Magnetism and electronic structure of PrNi_5 , ErNi_5 , LaCoO_3 and UPd_2Al_3 ” [2] describes well the general idea of our QUASST practical approach.

The aim of the present contribution is to point out the ongoing “revolution” in the theoretical description of transition-metal oxides, their low-energy electronic structure and the origin of magnetism, pointing more to the importance of local on-site effects like spin-orbit coupling in iridates [1]. Simultaneously, there is a “revolution” in understanding the exotic heavy-fermion phenomena, leaving dominant hybridization/mixed valence mechanisms for localized Ce^{3+} and Yb^{3+} CEF Kramers-doublet ground states, even in so famous h-f compounds as CeCu_2Si_2 [8] and YbRh_2Si_2 [3, 9, 10].

The author welcomes these two revolutions with great attention, because already 25 years ago he pointed out the importance of ionic crystal field (CEF) states and relativistic spin-orbit (s-o) effects in $3d$ oxides [11–14] despite the fact that the s-o interactions in $3d$ ions are rather weak. The existence of the discrete low-energy

CEF-like electronic structure in intermetallics such as $\text{Ho}_2\text{Co}_{17}$ and ErNi_5 was experimentally confirmed 35 years ago [4, 5].

The QUASST theoretical approach, starting from the atomic physics with the importance of the crystal field and the intra-ionic spin-orbit coupling, is basically different from the main-stream theoretical approaches, which from the beginning underline the solid-state effects, the substantial hybridization of cation $3d$ and oxygen $2p$ states and energy-continuous electronic structure spread over 1–4 eV.

2. Theoretical outline

In QUASST we claim that:

- (i) conventional crystal-field interactions should be evaluated first for any meaningful description of magnetic and electronic properties of any transition-metal (TM) $3d/4f/5f/4d/5d$ compound;
- (ii) in a TM compound there exists a discrete spin-orbital electronic structure at the energy scale, often below 1 meV;
- (iii) open-shell d electrons exhibit a substantial localized character, forming strongly-correlated d^n configurations and with largely integer occupation of t_{2g} and e_g states;
- (iv) intra-atomic relativistic spin-orbit interactions are indispensable for the physically-adequate description of the low-energy spin-orbital electronic structure of the involved TM ion;
- (v) this on-site, low-energy spin-orbital electronic structure largely determines the magnetic and electronic properties of the whole TM compound;
- (vi) standard band structure calculations, performed usually in the eV-energy scale should be completed with this discrete low-energy atomic-scale electronic structure with the indispensable consideration of the on-site spin-orbit interactions.

Concluding, QUASST is a phenomenological theory oriented to the experiment. It is, somehow, a long-term scientific project that helps experimentalists to build a consistent picture of transition-metal compounds. The formation of the title oxides and the realized valences can be inferred assuming the O^{2-} ions. The existence of Co^{2+} , Co^{3+} , V^{4+} , Ir^{4+} , and Ru^{4+} ions is confirmed by different experiments.

3. Some experimental facts

Here we mention some important experimental facts about CeRh_2Si_2 and the title oxides.

CeRh_2Si_2 , called in [15–17] Kondo-lattice intermetallics, exhibits an antiferromagnetic order below T_N of 36 K. In [16], the authors re-measured the temperature dependence of the specific heat, $c(T)$,

and evaluated the $4f$ contribution, $c_{4f}(T)$. Two literature models were used, including hybridization and Kondo effects, but did not manage to describe the $c_{4f}(T)$ contribution. In particular, those models completely did not account for the λ -type peak at T_N .

K_2CoF_4 crystallizes in the tetragonal K_2NiF_4 structure and exhibits an antiferromagnetic order below 97 K with a significant magnetic moment, above $3.2 \mu_B$, oriented along the tetragonal axis.

LaCoO_3 has a perovskite structure and exhibits peculiar magnetic properties. The temperature dependence of the paramagnetic susceptibility $\chi(T)$ exhibits a maximum about 95 K with the decrease of $\chi(T)$ to zero value with lowering temperature. It does not order magnetically, indicating the disappearance of the local cobalt moment at the absolute zero temperature. Such a disappearance is a surprise due to the strong magnetism of Co metal and many Co oxides.

Sr_2VO_4 exhibits a largely temperature-independent paramagnetic susceptibility, though with some anomalies. Such behavior of $\chi(T)$ resembles Pauli-like behavior and, as a consequence, itinerant band descriptions, rejecting the ionic V^{4+} state with one spin $S = 1/2$, were often applied. In 2009, Jackeli and Khaliullin pointed out [18] (this was their second paper that started the “revolution”) that such a nonmagnetic state of Sr_2VO_4 is an effect of local s-o interactions causing the spin moment $S = 1/2$ to be cancelled by the orbital moment $1 \mu_B$ [18]. We noticed such s-o effect for the d^1 ion already in 1999 in [11], where the zero magnetic moment is shown for the calculated lowest ground state.

Ba_2IrO_4 and Sr_2RuO_4 are oxide with $5d$ (Ir) and $4d$ (Ru) ions. Ba_2IrO_4 is an antiferromagnet with $T_N = 240$ K. There is a discussion about the charge state of iridium, being part of a very general problem about the relation between formal and realized charge and the valence state. The authors of [19] considering the hybridization $d-p$ model came to the exotic charge valences in Ba_2IrO_4 as $\text{Ba}_2^{1.5+}\text{Ir}^{2.65+}\text{O}_4^{1.4-}$ — it was one of a reason for remembering the ionic QUASST model underlying integer valences. In contrary to Ba_2IrO_4 Sr_2RuO_4 does not order magnetically down to the lowest temperatures, but below 2 K it exhibits superconductivity. Apart of the theoretical problem related to the occurrence of the superconductivity, there is the problem why the Ru ion loses its magnetic moment.

4. Some QUASST results and discussion

The low-temperature dependence of the specific heat of CeRh_2Si_2 has been recently re-measured in [16]. Contrary to these authors [16] who used two literature models with hybridization and Kondo effects, we managed to describe the magnetic

contribution $c_{4f}(T)$ in the whole measured temperature region (1–300 K) as associated with Ce^{3+} ions [20]. A finger print of the Ce^{3+} ions in the tetragonal structure is a 3 Kramers-doublet discrete CEF-like electronic structure, at about 39 ± 9 meV and 57 ± 5 meV. Hybridization/Kondo models that consider these doublet states as energetically broadened by 3 meV (thermal equivalence of the single-ion Kondo temperature) were completely unable to account for the $c_{4f}(T)$ dependence in the magnetic state, including the λ -type peak at T_N [16]. Our good reproduction of the λ peak at T_N proves that Kramers-doublet splitted states of the spin gap are energetically sharp within 0.2 meV [20]. In the magnetic state, below T_N of 36 K, the Kramers doublet ground state becomes split, opening a spin gap reaching 6 meV at $T = 0$ K. A good reproduction of the overall released entropy in the 1–300 K temperature range proves that practically all (at least 98%) Ce ions are in the trivalent state and contribute equally to the magnetic specific heat. The observed magnetic moment is basically of atomic origin.

The magnetic and electronic properties of K_2CoF_4 are well accounted for by Co^{2+} ions in the high-spin $3d^7$ configuration, i.e., $t_{2g}^5 e_g^2$ [21]. The derived CEF electronic structure containing doublet-quartet states of the lowest CEF subterm ${}^4T_{1g}({}^4F)$, fully accounts for both the value of the magnetic moment $3.25 \mu_B$ and its direction along the tetragonal axis [21]. Reproduction of the observed magnetic moment is possible when intra-ionic spin-orbit coupling is taken into account. The calculated magnetic moment is built up from the spin moment of $2.19 \mu_B$ and the orbital moment of $1.06 \mu_B$. The orbital moment is very large, reaching 1/3 of the total moment.

Magnetism of $LaCoO_3$ is completely different from K_2CoF_4 . In $LaCoO_3$, the Co ions are in the trivalent state as one can infer from simple ionic considerations. The Co^{3+} ion, being a non-Kramers ion, completely loses its magnetic moment being in the low-spin state $t_{2g}^6 e_g^0$ [7]. This low-spin state is the effect of a strong octahedral crystal-field acting on the Co ion from the oxygen octahedron. We have proved that the strong CEF interactions split the 13-fold degenerated 1I atomic term and push down the ${}^1A_{1g}$ singlet subterm, which can be traced on the Tanabe–Sugano diagrams. This ${}^1A_{1g}$ singlet decreases its energy fast due to a large orbital moment (the 1I term has $S = 0$ and $L = 6!!$).

The comparison of K_2CoF_4 and $LaCoO_3$ allows for the study of the formation of the local Co magnetic moment by means of different charge state, different local symmetry and different strength of the crystal-field and spin-orbit interactions.

Sr_2VO_4 is a nice manifestation of the fundamental role of the spin-orbit coupling in $3d$ ions, though its value is only 30 meV. The spin-orbit coupling causes almost perfect compensation of the spin moment by the orbital moment.

Ba_2IrO_4 and Sr_2RuO_4 are now described as having Ir^{4+} and Ru^{4+} ions coming out from ionic considerations. These ions take the low-spin configurations t_{2g}^5 and t_{2g}^4 — details of the low-energy electronic structure come out from the crystal-field considerations. Many of them have been overviewed in the text-book of Abragam and Bleaney [22] published already in 1970 for the description of paramagnetic impurities in oxides. According to QUASST, the nonmagnetic state of Sr_2RuO_4 , which persists down to 2 K when the superconducting state is unexpectedly formed, is associated with the detailed spin-orbital Ru^{4+} ionic electronic structure. The Ru^{4+} ion is a non-Kramers ion, and the singlet (nonmagnetic) ionic ground state is produced from the 9-fold degenerated ${}^3T_{1g}$ subterm by a crystal-field (tetragonal lattice distortion) and intra-ionic spin-orbit coupling. This singlet becomes weakly magnetized by the hybridization with the excited magnetic doublet forming a background for magnetically-driven superconductivity.

Inspecting the recent $NdNiO_2$ literature, we just noticed that the authors of [23] discussing the novel superconductor $NdNiO_2$ without any explanation write Nd^{3+} and (very rare configuration) Ni^{1+} ions. This means that after 20 years, QUASST is indeed already widely used. We also noticed that our approach is in the spirit of the scientific groups of Sawatzky [24, 25], of Katukuri/van den Brink/Hozoi [26], and of Millis [27] — their impurity calculations include the full Ni^{2+} ($3d^8$)-ion multiplet structure. Both of these groups deduced the excitations energy spectra of the Ni^{1+} ($3d^9$)-ion starting from conventional CEF, spin-orbit coupling and lattice distortions. It is useful if theoreticians present results that can be experimentally verified.

5. Conclusions

The description of $CeRh_2Si_2$ (and earlier Ho_2Co_{17} and $ErNi_5$ of many other intermetallics) proves that the CEF states exist in the compounds' "conducting current". In oxides, the realized cation valency is basically equal to the formal valency from the ionic model. Such treatment of NiO , $LaCoO_3$, and many other oxides was highly criticized 10–20 years ago, but in the present literature such integer valency is "simply taken without any explanation". The realized valency can be experimentally verified by having its own finger print in the excitation spectrum. Even weak spin-orbit interactions in the $3d^1$ -ion oxides are responsible for violation of the Curie–Weiss law at low temperatures, and often for the realization of the nonmagnetic state, especially for non-Kramers ions, as it is in case of Sr_2RuO_4 .

The methodology of quantum atomistic solid-state theory (QUASST) "From atomic physics to solid-state physics" is very fruitful and offers a consistent picture of transition-metal compounds. The

author realizes this project practically throughout his whole long scientific life and has the scientific satisfaction that better experiments and better samples largely confirm the conventional mathematical concepts of physics.

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