Charge and crystal field electronic states in CeRh$_2$Si$_2$ and Ba$_2$IrO$_4$

R. J. RADWANSKI$^{1,2}$, D. M. NALECZ$^1$ and Z. ROPKA$^2$

$^1$Institute of Physics, Pedagogical University, 30-084 Krakow, Poland
$^2$Center of Solid State Physics, Snt Filip 5, 31-150 Krakow, Poland
E-mail: sfradwan@cyf-kr.edu.pl

Abstract. We point out the scientific importance of the increasing evidence for the existence of the discrete low-energy meV-energy states in compounds containing atoms with incomplete 4f, 5f, 3d shells and recently in iridates (5d shell). We point out that the realized charge state of the 3d/4f/5f/4d/5d atoms/ions in oxides is very close to the formal one obtained within the ionic model. In Ba$_2$IrO$_4$ the charge states are very close to Ba$^{2+}$, Ir$^{4+}$ and O$^{2-}$. In CeRh$_2$Si$_2$, which is intermetallic and considered as a Kondo-lattice antiferromagnet, by detailed analysis of temperature dependence of the specific heat we have proved the realization of the trivalent charge state of practically all cerium ions. In the magnetic state, below T$_N$ of 36 K, the Kramers doublet becomes split and there appears a spin gap growing to 6 meV at T= 0 K.

1. Introduction
Description of magnetic and electronic properties of compounds containing 3d-/4f-/5f-open-shell atoms has been very vital part of the condensed-matter physics in last fifty years. The interest has been associated with such topics as Mott insulators, NiO [1], FeBr$_2$ [2] or LaCoO$_3$ [3], and heavy-fermion anomalous phenomena occurring in intermetallics with Ce, Yb and uranium (UPd$_2$Al$_3$ [4]) atoms. These anomalous properties are very different from classical behavior observed in, e.g. ErNi$_5$ [5], Ho$_2$Co$_{17}$ [6], Nd$_2$Fe$_{14}$B [7] intermetallics. CeRh$_2$Si$_2$ is considered as a Kondo-lattice antiferromagnet with T$_N$ of 36 K [8]. Recently iridates with open 5d shell like Sr$_2$IrO$_4$ [9] and Ba$_2$IrO$_4$ [10], enter to the experimental and theoretical field.

The aim of the present contribution is a problem of formal and realized charge states in compounds containing open-shell atoms/ions.

2. Formal and real charge state in Ba$_2$IrO$_4$
Each theoretical study practically starts with an assumption/a concept about the charge state of the open-shell atoms constituting a considered compound on basis of experimental facts about its electronic and magnetic properties. In literature there is discussion about the role of 3d-/4f-/5f-/4d-/5d— (we sometimes will call all these atoms/ions as transition-metal atoms/ions) open-shell electrons - should they be described as itinerant or localized? We are strongly localized. In fact, such question should be formulated rather as the localized or the itinerant/band model is a better starting point for the physically adequate theoretical description of electronic and magnetic properties, remembering also about different temperature regions.
Our description of Ba$_2$IrO$_4$ starts with the ionic model. It demands the tetravalent Ir charge state. Such starting point, quite obvious to experimentalists, is in sharp contrast to results of a quite recent publication [11] in Phys. Rev. B in which authors have claimed that in Ba$_2$IrO$_4$ the valency of Ba is 1.5+ (in contrast to the expected charge state of 2+) and iridium of 2.32+ only (instead of the expected 4+). We are strongly localized, i.e. we think that a number of valence electrons in the open electronic shell should be close to the integer number. Authors of the recalled paper have strongly stated that accepting the charge state in oxides on basis of the ionic model, called by these authors as ”naive”, is completely erroneous as the real charge state is largely different. Authors of the recalled paper, in the developed $d - p$ model, have assumed substantial oxygen hybridization and very strange barium valence as Ba$^{1.5+}$. In a consequence they rejected ”the idealistic formal ionic model” accepting Ba$^{1.5+}$ and Ir$^{2.32+}$ ionic states.

The publication of so exotic theoretical results in Phys. Rev. B proves the scientific necessity of the formulation of reasonable and physically adequate Quantum Atomistic Solid State theory (QUASST) [1, 12]. QUASST points the substantial preservation of the ionic integrity and importance of the local effects, like the crystal field (CEF) and the spin-orbit (s-o) coupling. An experimental hallmark of QUASST is observation, apart of the large 5-100 eV multiplet electronic structure, of the quasi-atomic discrete electronic structure in the meV-energy scale. QUASST underlines that the strong electron correlations are predominantly of the on-site atomistic/ionic origin. We claim that in Ba$_2$IrO$_4$ the charge distribution is very close to the ionic, Ba$^{2+}$, O$^{2-}$ and Ir$^{4+}$. The multiple electronic structure observed in Ba$_2$IrO$_4$ at neighborhood of 0.6 eV, originating from large intra-atomic spin-orbit coupling, is a finger print of the tetravalent iridium charge state.

3. Formal and real charge state in intermetallics: CeRh$_2$Si$_2$

Determination of the charge state of all atoms in intermetallic is rather problematic in comparison to oxides/fluorines. However, one of us (RR) already in 1984 has applied, working at the University of Amsterdam in the group of Prof. J. J. M. Franse, the crystal-field theory to METALLIC Ho$_2$Co$_{17}$ [6]. By successful description of its electronic and magnetic properties we have proved the existence of the Ho$^{3+}$ ions in this intermetallic system. Later low-energy crystal field states, energies and eigenfunctions, associated with Er$^{3+}$ and Nd$^{3+}$ ions have been described in conventional ErNi$_5$ [5] and Nd$_2$Fe$_{14}$B [7] intermetallics. An our description of normal-state electronic and magnetic properties of UPd$_2$Al$_3$ [4], above the heavy-fermion and superconducting states (above, say 3 K) with U$^{3+}$ ions was later confirmed by experimental discovery of CEF states in inelastic-neutron scattering experiments [13]. The U$^{3+}$ ion has the Kramers doublet ground state. Then in year of 1992 one of us (RR) stated that the heavy-fermion phenomena are largely associated with a difficulty in removing the Kramers degeneracy in trivalent Ce, Yb and U intermetallics (abstract at the 1st SCES-92 Conf. Sendai-92: R. J. Radwanski, ”Formation of the heavy-fermion state - an explanation in a model traditionally called localized” poster 8P-92 SCES-1992, Sendai-92).

It is worth to remind that it was time (1980-2010) that such concepts like ionic states in intermetallics, CEF in heavy-fermion intermetallics, s-o coupling in 3d oxides, discrete states, below, say, 10 meV, in 3d oxides) have been treated as scientific heresies. We underline the existence of the crystal-field quasi-atomic states in these metallic systems having in mind, apart of subsequent rejections at SCES Conf., an administration decision of the Polish Highest Scientific Committee (BCK-V-P-1262/02, 2003) that ”applying the crystal-field theory to compounds conducting current is erroneous” [14]). The obvious nonsense, but such nonsense postponed the real professor scientific carrier by 10 years - it documents that the existence of crystal-field ionic states and discrete low-energy electronic structure in intermetallics was not obvious as it is at present. This scientific situation has radically changed after the
discovery in the group of Prof. Frank Steglich, of the ionic Yb\textsuperscript{3+} state and its the Kramers-doublet ground state in the profound heavy fermion YbRh\textsubscript{2}Si\textsubscript{2} \cite{15}. The electron spin resonance has been observed at 1.5 K, i.e. deeply in the Kondo/heavy-fermion state owing to its Kondo temperature $T_K$ of 25 K.

![Figure 1](https://example.com/fig1.png)

**Figure 1.** The calculated, within the CEF-based QUASST approach, temperature dependence of the 4\textit{f} electron (magnetic+CEF) contribution, originating from localized crystal-field states of the Ce\textsuperscript{3+} ion, to the specific heat (left) and to the entropy (right) of CeRh\textsubscript{2}Si\textsubscript{2} (thick solid red line with a peak at $T_N$ at 36 K) together with experimental data (black dots), reported by Patil \textit{et al.} \cite{16} and with their three theoretical calculations (thin lines). Coloured thin lines show the curves calculated by Patil-16 \cite{16} for different values of the CEF splitting, of the Kondo temperature $T_K$, and of the width $\Gamma_i$ of the first excited CEF level. Patil-16 results have been calculated with parameters: $T_K = 3.0$ meV, $\Gamma_1 = 5.1$ meV, $\Delta_1 = 48$ meV and $\Delta_2 = 62$ meV - solid magenda line; 3.0, 5.1, 30 and 52 meV - solid blue line, and 0.3, 15, 30 and 52 meV - dashed green line. Colours are the same as in the original paper of Patil-16. In the inset the calculated splitting of the Kramers doublet below $T_N$ and the opening of the spin gap is shown.

CeRh\textsubscript{2}Si\textsubscript{2}, isostructural to YbRh\textsubscript{2}Si\textsubscript{2}, has been considered as a Kondo-lattice antiferromagnet with $T_N$ of 36.5 K \cite{16}. XAS \cite{8}, ARPES \cite{16} and RIXS \cite{17} experiments revealed two CEF states at 30/48 and 52/62 meV, respectively, expected for the $4f^1$ configuration in the tetragonal symmetry confirming earlier CEF findings on basis of classical magnetic measurements \cite{18, 19}. Apart of ARPES experiment Patil \textit{et al.} \cite{16} [later denoted as Patil-16] have tried to describe the temperature dependence of the specific heat. For the theoretical description of $4f$ contribution $c_{4f}(T)$ they have used two literature models both taking into account the hybridization and Kondo interactions. Despite of taking very different parameters they did not get a satisfactory description below 150 K. Moreover, their description of $c_{4f}(T)$ and the involved entropy $S_{4f}(T)$ below Neel temperature was completely wrong, as one can see on Fig. 1. Our crystal-field based QUASST description \cite{20} very well describes $c_{4f}(T)$ and $S_{4f}(T)$ in the whole temperature range, from zero up to measured 300 K, together with very good description below $T_N$. A $\lambda$-type peak at 36 K is also nicely reproduced.

Good description below $T_N$ of 36 K (=3 meV) confirms that CEF states in CeRh\textsubscript{2}Si\textsubscript{2} are remarkably thin (in the energy scale their width is lower than 0.3 meV) and that practically all
Ce atoms/ions contribute to the experimental specific heat. An obtained value of the molecular-field coefficient of 19 T/\mu_B indicates that each Ce ion experiences the molecular field of 30 T. This value is close to value of 26 T at which the antiferromagnetic structure is broken by external magnetic field [21]. Our model predicts, in contrary to models used in Ref. [16], opening of a spin gap in the antiferromagnetic state, see inset in Fig. 1. Its value grows to 6 meV at T=0 K. We think that appearance of such gap should be experimentally verified.

In conclusion, we have established the charge state of iridium in Ba$_2$IrO$_4$ as Ir$^{4+}$ and of cerium in CeRh$_2$Si$_2$ as Ce$^{3+}$. Our results are in agreement with realization of different integer valences in rhenium [22] and osmium [23, 24] oxides. Good description below $T_N$ of 36 K (=3 meV) confirms that CEF states in CeRh$_2$Si$_2$ are remarkably thin (in the energy scale their width is lower than 0.3 meV) and that practically all Ce atoms/ions contribute to the experimental low-temperature specific heat. We conclude that hybridization/mixed valence phenomena are very weak in CeRh$_2$Si$_2$.

References
[1] Radwanski R J and Ropka Z 2000 Acta Phys. Pol. A 97 963; 2006 Acta Physica 1 26; [arXiv:0606604].
[2] Ropka Z, Michalski R and Radwanski R J 2001 Phys. Rev. B 63 172404
[3] Ropka Z and Radwanski R J 2003 Phys. Rev. B 67 172401
[4] Radwanski R J, Nalecz D M and Ropka Z 2016 Acta Phys. Pol. A 130 545
[5] Radwanski R J, Kim-Ngan N H, Kayzel F E, Franse J J M, Gignoux D, Schmitt D and Zhang F Y 1992 J. Phys.: Condens. Matter 4 8853
[6] Franse J J M, de Boer F R, Frings P H, Gersdorf R, Menovsky A A, Muller F A, Radwanski R J and Sinnema S 1985 Phys. Rev. B 31 4347
[7] Radwanski R J and Franse J J M 1989 J. Magn. Magn. Mater. 80 14
[8] Willers T, Adroja D, Rainford B, Hu Z, Hollmann N, Konner P, Chin Y -Y, Schmitz D, Hsieh H, Lin H -J, Chen C T, Bauer E D, Sarrao J L, McClellan K J, Byler D, Geibel C, Steglich F, Aoki H, Lejay P, Tanaka A, Tjeng J H and Severing A 2012 Phys. Rev. B 85 035117
[9] Bertinshaw J, Kim Y K, Khaliullin G and Kim B J, Annu. Rev. Condens. Matter Phys. 2019 10 315 Bertinshaw J, Kim J K, Porras J, Ueda K, Sung N H, Efimenko A, Bombardi A, Jungho Kim, Keimer B and Kim B J 2020 Phys. Rev. B 101 094428
[10] Moser S, Moreschini L, Ebrahimi A, Dalla Piazza B, Isobe M, Okabe H, Akimitsu J, Mazurenko V V, Kim K S, Bostwick A, Rotenberg E, Chang J, Ronnow H M and Grioni M 2014 New J. Phys. 16 013008
[11] Rosciszewski K and Oles A M 2016 Phys. Rev. B 93 085106
[12] Radwanski R J, Michalski R and Ropka Z 2000 Acta Phys. Pol. B 31 3079; Radwanski R J, Michalski R and Ropka Z 2000 Physica 276-278 803
[13] Krimmel A, Loi A, Eccleston R, Geibel C and Steglich F 1996 J. Phys.: Condens. Matter 8 1677
[14] Radwanski R J 2008 Acta Physica 12-13 1; 2008 16-17 1
[15] Sickelschmidt J, Ivanovshin V A, Fersht J, Geibel C and Steglich F 2003 Phys. Rev. Lett. 91 156401
[16] Patil S, Generalov A, Guttler M, Kushwaha P, Chikina A, Kummer K, Rodel T C, Santander-Syro A F, Caroca-Canales N, Geibel C, Danzenbacher S, Kucherenko Y, Laubacht, Allen C, Ellen J W and Vyalikh D V 2016 Nat. Commun. 7 11029
[17] Amorese A, Caroca-Canales N, Seiro S, Krellner C, Ghiringhelli G, Brookes N B, Vyalikh D V, Geibel C and Kummer K 2018 Phys. Rev. B 97 245130
[18] Knafo W, Aoki D, Vignolles D, Vignolle B, Klein Y, Jaudet C, Villanne A, Proust C and Flouquet J 2010 Phys. Rev. B 81 094403
[19] Settai R, Misawa A, Araki S, Kosaki M, Sugiyama K, Takeuchi T, Kindo K, Haga Y, Yamamoto E and Onuki Y 1997 J. Phys. Soc. Jpn 66 2260
[20] Radwanski R J, Z. Ropka and D. M. Nalecz 2019 Mater. Chem. Phys. 232 301
[21] Abe H, Kitazawa H, Suzuki H, Kido G and Matsumoto T 1998 Physica B 246-247 141; Abe H, Kitazawa H, Suzuki H, Kido G and Matsumoto T 1998 J. Magn. Magn. Mater. 177-181 479
[22] Hirai D and Hiroi Z 2021 J. Phys.: Condens. Matter 33 135603
[23] Erickson A S, Misra S, Miller G J, Gupta R R, Schlessinger Z, Harrison W A, Kim J M and Fisher I R 2007 Phys. Rev. Lett. 99 016404
[24] Paramekanti A, at this SCES-20 Conference