Unusually Short Ce–Ru Distances in CeRuAl and Related Compounds

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The aluminide CeRuAl with orthorhombic LaNiAl-type structure contains two crystallographically independent cerium sites which both exhibit relatively short Ce–Ru distances, *i. e.* 280 – 302 pm for Ce1 and 286 – 310 pm for Ce2. Susceptibility measurements show intermediate valence behavior of the cerium atoms (1.19(1) μ_B per formula unit) and no magnetic ordering down to 2 K. Chemical bonding analysis reveals a non-magnetic ground state and strong Ce–Ru bonding. The Ce–Ru bonding peculiarities of CeRuAl are discussed in line with those of other binary and ternary cerium–ruthenium compounds.

Key words: Cerium, Ruthenium, Intermediate Valence, Magnetic Properties, Electronic Structure

Introduction

Intermetallic cerium compounds have widely been investigated in the last 40 years with respect to their intriguing physical properties [1]. This is due to the peculiar valence behavior, *i. e.* trivalent cerium has a [Xe]4f^1 configuration and exhibits paramagnetism (often accompanied by magnetic ordering), while tetravalent cerium, [Xe]4f^0, is diamagnetic. Many of these cerium compounds exhibit either static or dynamic intermediate cerium valence. Various examples are known where the cerium valence can be influenced by temperature [2, 3], by pressure [4], or upon hydrogenation [5].

A somewhat unique bonding situation arises for intermediate-valent cerium in combination with ruthenium as the transition metal component. In the five binary compounds [6] Ce_3Ru [7], Ce_7Ru_3 [7, 8], $Ce_{16}Ru_9$ [7, 9], Ce_4Ru_3 [7, 10], and $CeRu_2$ [11], several Ce–Ru distances (Table 1) are significantly shorter than the sum of the covalent radii [12] of 289 pm. Such short Ce–Ru distances can only be explained by the presence of *small*, *i. e.* partially tetravalent cerium atoms. Indeed, magnetic susceptibility and XPS data revealed intermediate cerium valence in $CeRu_2$, $Ce_{16}Ru_9$, and Ce_7Ru_3 [13 – 17]. Among these binaries, $CeRu_2$ shows superconductivity below 6.2 K [13].

Even shorter Ce–Ru distances, down to 223 pm, have recently been observed in a variety of cerium–ruthenium–indides, *i. e.* $Ce_3Ru_2In_3$ [18], $Ce_{16}Ru_8In_{37}$ [19], $Ce_2Ru_2In_3$ [20], $Ce_3Ru_2In_2$ [20], and $CeRu_{0.88}In_2$ [21]. However, intermediate cerium valence has not been proven experimentally. Static mixed cerium valence in CeRuSn [22, 23] and Ce_2RuZn_4 [24, 25] has been confirmed by crystal structure determination, electronic structure calculations as well as temperature-dependent susceptibility measurements. Both compounds contain one discrete Ce^{III} and one $Ce^{\sim IV}$ site. The latter shows very short Ce–Ru distances, and susceptibility measurements reveal a paramagnetic moment only on the Ce^{III} site. The Ce^{III} site in Ce_2RuZn_4 orders antiferromagnetically at T_N = 2.1 K [25].

Since these unusually short Ce–Ru distances seem to be a key feature in intermetallic compounds with comparatively high contents of cerium and ruthenium, and since these peculiarities are often accompanied by exciting physical properties, we have started a systematic study of the structure-property relations of such ternary cerium intermetallics. The so far most complex system is $Ce_{23}Ru_7Cd_4$ [26]. This structure contains nine crystallographically independent cerium sites. Five cerium sites in $Ce_{23}Ru_7Cd_4$ show Ce–Ru distances which are shorter than the Pr–Ru distances in $Pr_{23}Ru_7Cd_4$. $Ce_{23}Ru_7Cd_4$ shows an average, reduced magnetic moment of 2.05 μ_B/Ce atom. The trivalent cerium atoms undergo ferro- or ferrimagnetic ordering below T_C = 3.6 K. Isotypic $Ce_{23}Ru_7Mg_4$ [27] shows similar behavior.

Herein we report on the magnetic properties and chemical bonding of CeRuAl. In first reports [28], this compound was studied by powder diffraction, and the structure of the hexagonal Laves phase with statistical Ru/Al occupancy was assigned. Later on a single crystal study [29] revealed the completely ordered orthorhombic LaNiAl type with short Ce–Ru distances in the range 280 – 310 pm, and the authors suggested dimorphism for this equiatomic compound.

Experimental Section

Synthesis

Starting materials for the synthesis of CeRuAl were a cerium ingot (smart elements), ruthenium powder (Degussa-Hüls, *ca.* 200 mesh), and aluminum turnings (VAW), all with stated purities better than 99.9 %. Pieces of the cerium ingot, a cold-pressed pellet (∅ 6 mm) of the ruthenium powder and pieces of the aluminum turnings were weighed in 36 : 32 : 32 stochiometry and arc-melted [30] under an argon pressure of *ca.* 800 mbar. The button was remelted three times to ensure homogeneity. CeRuAl is stable in air for months. Additionally, two samples of the starting compositions 1Ce : 1.15Ru : 0.85 Al and 1Ce : 0.85Ru : 1.15 Al were prepared under the same conditions.

EDX data

Semiquantitative EDX analyses on all bulk samples were carried out by use of a Leica 420i scanning electron microscope with the rare-earth trifluorides, CeO_2, ruthenium, and aluminum as standards. The polycrystalline samples were embedded in a methylmethacrylate matrix and polished with different diamond and SiO_2 emulsions. The experimentally observed compositions were close to the ideal one. No impurity elements heavier than sodium (detection limit of the instrument) were observed.

X-Ray powder diffraction

The polycrystalline samples were characterized by Guinier patterns (imaging plate detector, Fujifilm BAS-1800) with Cu$K_{\alpha 1}$ radiation and α-quartz (a = 491.30, c = 540.46 pm) as an internal standard. Correct indexing of the diffraction lines was ensured through intensity calculations [31]. The lattice parameters were obtained through least-squares fits.

Magnetic measurements

The CeRuAl sample was packed in kapton foil and attached to the sample holder rod of a VSM for measuring the magnetic properties in a Quantum Design Physical-Property-Measurement-System in the temperature range 2 – 300 K with magnetic flux densities up to 80 kOe.

Computational details

The electronic structure calculations for CeRuAl were performed using the augmented spherical wave (ASW) method [32, 33] built within the density functional theory (DFT) framework [34, 35]. All valence states were treated as band states. In the minimal ASW basis set, the outermost shells were chosen to represent the valence states using partial waves up to $l_{max} + 1 = 4$ for Ce, and $l_{max} + 1 = 3$ for Ru and Al. The completeness of the valence basis set was checked for charge convergence, *i. e.* less than 0.1 electrons for $l_{max} + 1$. The self-consistent field calculations were run to a convergence of 10^{-8} for the charge density, and the accuracy of the method is in the range of about 10^{-8} Ryd. (1 Ryd. = 13.6 eV) regarding energy differences. The effects of exchange and correlation were treated based on the local density approximation LDA [36]. Spin degenerate, nonmagnetic (NM) calculations were carried out for the analysis of chemical bonding. Then spin-polarized (SP) calculations were done to check for the possible onset of ordered magnetic moments of the constituent species. We note here that a NM configuration does not correspond to the paramagnetic one which could be achieved for instance by using supercells with random spin orientations.

The analysis of the chemical bonding pertains to the information on the nature of the interactions between the atomic constituents. From electronic structure calculations, this can be obtained by examining the crystal orbital overlap population (COOP) introduced by Hoffmann [37] in extended Hückel-type calculations and later on implemented within the ASW code [38]. In short hand notation, avoiding extended equations, the COOP can be looked at as the DOS weighted by the overlap integral S_{ij} between two chemical species i and j. They carry the same unit as the DOS of inverse energy (1/eV). In the plots, positive, negative and zero magnitudes of COOP are indicative of bonding, antibonding, and nonbonding interactions, respectively.

Discussion

Phase analyses and crystal chemistry

A LaNiAl-type sample of CeRuAl was crystallized directly from the melt. The sample (36 : 32 : 32 starting composition) was almost phase-pure. Only a trace amount of elemental ruthenium could be detected by EDX and X-ray powder diffraction. The melting of a starting composition 1 : 1 : 1 leads to a mixture of RuAl, $CeRu_2$ and CeRuAl (LaNiAl type), most likely due to the strong phase stability of RuAl with CsCl-type structure. Therefore, a careful look into the phase diagram predicts the starting composition 36 : 32 : 32 to avoid the RuAl side phase. The refined lattice parameters of our sample (a = 721.8(2), b = 406.4(2), c = 1590.6(8) pm, V = 0.4666 nm^3) are in agreement with the data given by Gribanov *et al.* (a = 720.7(1), b = 405.06(8), c = 1586.6(3) pm, V = 0.4632 nm^3) [29]. Since we obtained the sample directly *via* solidification of the melt, and since the annealed sample prepared by Gribanov *et al.* [29] also crystallizes with the same structure type, we suppose that the samples reported to have the structure of the hexagonal Laves phase $MgZn_2$ [28] most likely have slightly different compositions. If some of the ruthenium remains unreacted (this often occurs as a consequence of the high melting point), an aluminum-rich solid solution $CeRu_{1-x}Al_{1+x}$ with the Laves phase structure is formed.

Additional samples with the starting compositions 1Ce : 1.15Ru : 0.85 Al and 1Ce : 0.85Ru : 1.15 Al were prepared in order to check this behavior. Indeed, the 1Ce : 0.85Ru : 1.15 Al sample showed the structure of the hexagonal Laves phase with refined lattice parameters of a = 551.4(2) and c = 871.5(3) pm, V = 0.2294 nm^3, close to the lattice parameters of a = 550.5 and c = 870.0 pm (the lattice parameter c of 807.0 pm given in that report is most likely a transposed digit) for the 'CeRuAl' sample given in [28]. In contrast, the Guinier powder pattern of the 1Ce : 1.15Ru : 0.85 Al sample revealed only a small amount of the LaNiAl-type phase besides mainly RuAl and $CeRu_2$. We therefore conclude that CeRuAl is a congruently melting compound that shows no dimorphism.

CeRuAl crystallizes with the orthorhombic LaNiAl-type structure [39]. Since the crystal chemistry of this structure type has already been discussed in detail also for LaRhMg [40], CeRhZn [41], and CeRuAl [29], here we give only a brief description and concentrate on the coordination polyhedra of the cerium sites only. In Fig. 1 we compare the coordination polyhedra of the two crystallographically independent cerium sites in the structures of CeRuAl and CeRuSn [22]. For all four sites we observe the Ce–Ru distances as the shortest ones. Also it is commom to these sites that each cerium atom has five nearest ruthenium neighbors, however, with somewhat different distance ranges. The Ce1 atom of CeRuSn which is almost tetravalent has a very short Ce–Ru distance of 233 pm, while the Ce–Ru distances of the Ce1 and Ce2 atoms of CeRuAl range from 281 to 314 pm. Nevertheless, the shorter ones are below the sum of the covalent radii [12] of 289 pm. These distances are responsible for the intermediate cerium valence discussed below. Interestingly, the Ce–Ce distances in both compounds are well above the Hill limit [42] of *ca.* 340 pm for f electron localization.

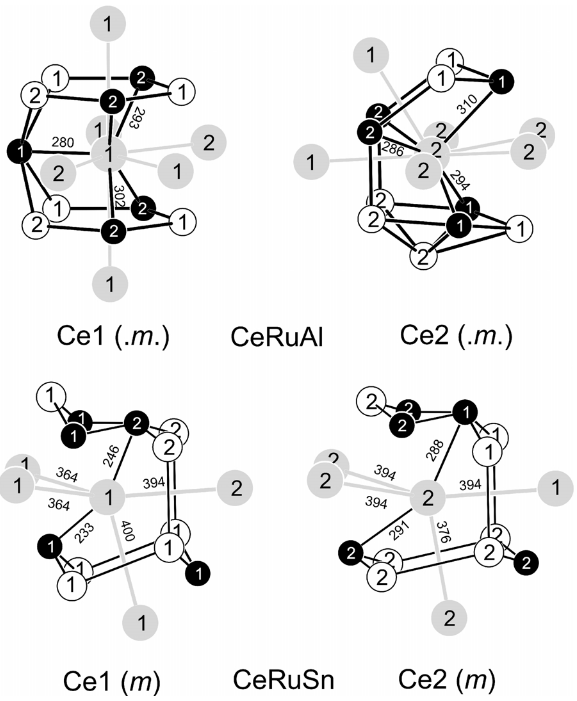


Fig. 1. Coordination polyhedra of the two crystallographically independent cerium sites in the CeRuAl [29] and CeRuSn [22] structures. Cerium, ruthenium, tin/aluminum atoms are drawn as light grey, black filled, open circles, respectively. Relevant interatomic distances and site symmetries are indicated.

In ternary compounds with a lower cerium content such as $Ce_3Ru_4Al_{12}$ [39, 43], $Ce_2Ru_3Al_{15}$ [44], $CeRu_2Al_{20}$ [45, 46], or $CeRu_4Sn_6$ [47] we no longer observe short Ce–Ru distances. Such structures are composed of complex three-dimensional $[Ru_yX_z]$ networks with strong covalent Ru–X bonding. The networks leave larger cages which are filled by the cerium atoms, and in all cases the Ce–Ru distances are longer than 300 pm.

In Table 1 we have listed those compounds which exhibit at least one short Ce–Ru distance, shorter than the sum of the covalent radii of 289 pm [12]. Except $CeRu_2$, all binary Ce–Ru compounds belong to this family. Due to the larger combinatorial variety, more

Table 1. Ce–Ru distances (pm) of the first coordination spheres for selected binary and ternary intermetallic compounds.

Compound	Atom	Ce–Ru distances
Ce_3Ru [7]	Ce1	298, 301, 338
	Ce2	261, 279
$Ce_{16}Ru_9$ [16]	Ce1	257 (2×), 292, 293
	Ce2	256 (2×), 313, 339
	Ce3	262 (2×), 293, 317, 360
	Ce4	307 (2×), 314 (2×), 320 (2×)
	Ce5	312 (2×), 325 (2×), 364 (2×)
	Ce6	346 (6×)
	Ce7	386 (6×)
Ce_7Ru_3 [8]	Ce1	294 (2×), 349 (2×)
	Ce2	282 (2×), 295, 367
	Ce3	299 (3×)
Ce_4Ru_3 [10]	Ce1	275, 297, 303, 305, 325, 326
	Ce2	275 (2×), 295, 305
	Ce3	275 (2×), 285 (2×), 287 (2×)
$CeRu_2$ [11]	Ce	312 (12×)
CeRuAl [29]	Ce1	280, 293 (2×), 302 (2×)
	Ce2	286 (2×), 294 (2×), 310
$Ce_3Ru_2In_3$ [18]	Ce1	238, 273, 330 (2×)
	Ce2	345 (2×)
$Ce_{16}Ru_8In_{37}$ [19]	Ce1	–
	Ce2	237 (2×)
	Ce3	–
$Ce_2Ru_2In_3$ [20]	Ce1	346 (2×), 349 (2×)
	Ce2	232, 237, 329 (2×)
$Ce_3Ru_2In_2$ [20]	Ce1	223, 286, 315 (2×)
	Ce2	351 (2×), 353, 364, 367 (2×)
	Ce3	228, 298, 333 (2×)
$CeRu_{0.88}In_2$ [21]	Ce	253, 336 (2×)
CeRuSn [22]	Ce1	233, 246, 330 (2×), 364
	Ce2	288, 291, 347 (2×), 362
Ce_2RuZn_4 [24]	Ce1	–
	Ce2	260 (2×)
$Ce_{23}Ru_7Cd_4$ [26]	Ce1	300 (2×), 361 (2×)
	Ce2	293 (2×), 301
	Ce3	258, 274
	Ce4	347 (2×)
	Ce5	289 (2×), 302
	Ce6	333, 356
	Ce7	301 (3×)
	Ce8	286 (3×)
	Ce9	275 (2×), 386

compounds with such structural peculiarities are expected for the ternary Ce–Ru–*X* systems. So far nine compounds have been structurally characterized. Systematic phase-analytical studies of such materials are currently under way in order to elucidate the interesting structure-property relations which are directly correlated with the intermediate cerium valence.

Magnetic properties

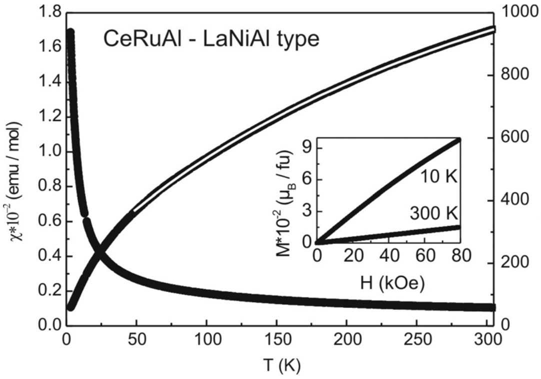


Fig. 2. Temperature dependence of the magnetic and inverse magnetic susceptibility of CeRuAl measured at 1 T. The white line presents the modified Curie-Weiss fit of $\chi^{-1}(T)$. The inset shows the magnetization isotherms at 10 and 300 K.

CeRuAl shows only a moderately temperature-dependent susceptibility (H = 10 kOe) (Fig. 2), which is typical for an intermediate-valent cerium compound. A fit of the susceptibility in the region 50 – 300 K according to a modified Curie-Weiss expression $\chi^{-1} = (\chi_0 + C/(T - \theta_p))^{-1}$ revealed a temperature-independent contribution χ_o = 5.3(1) × 10^{-4} emu mol^{-1}, a magnetic moment μ_{eff} = $(8C)^{1/2} = (8 \times 0.177)^{1/2}$ = 1.19(1) μ_B /*fu* and the paramagnetic Curie temperature θ_P = −32.5(2) K. Since the experimental magnetic moment is much smaller than the free ion value of 2.54 μ_B for Ce^{3+}, we can assume intermediate-valent cerium in CeRuAl (C = 0.177(1) emu K mol^{-1}, *i. e.* 22 % of the Ce atoms have a 4f electron). The magnetization isotherms (inset Fig. 2) at 10 and 300 K are almost linear with small magnetization values at the highest obtainable field of 80 kOe. This behavior is similar to that of isotypic CeRhAl [48 – 50].

It may also be noted here that mixed valency (one Ce site is purely trivalent and the second one is intermediate-valent) is neither possible for CeRuAl nor for CeRhAl as suggested by Kumar *et al.* [48, 49]. The calculated moments are 1.17 and 1.19 μ_B /*fu*, respectively. If one independent cerium site is in a trivalent state (a required citerion for mixed valence), the observed moment must be minimum 1.79 μ_B /*fu* [$\mu_{eff,min} = (2.54^2/2)^{1/2}$]. This fact clearly reveals that the cerium atoms in CeRuAl and CeRhAl on both independent crystallographic sites are in an intermediate valence state. Beside these LaNiAl-type compounds so far only two other Ce intermetallics with this structure type are known: CeRhMg [40] (no properties were determined) and CeRhZn. In the case of

CeRhZn, both cerium sites have almost tetravalent atoms [41].

Chemical bonding analyses

So far, studies of chemical bonding for such compounds with comparatively short Ce–Ru distances were only reported for CeRuSn [23] and Ce_2RuZn_4 [25]. Both studies showed extremely strong Ce–Ru bonding for the intermediate-valent (nearly tetravalent) cerium sites. In order to extend these investigations we have also studied chemical bonding in CeRuAl which shows similar structural features.

At self-consistent convergence little charge transfer was observed between the atoms. In such an intermetallic system it can be rather argued that the quantum mixing between the different valence states of the constituents is the underlying mechanism of bonding as it will be explained first from the site-projected density of states (PDOS) and from an analysis of the chemical bonding based on overlap populations.

In Fig. 3, showing the site-projected density of states (PDOS) for CeRuAl, the Fermi level (E_F) is taken as zero energy. This is also done in the following plots describing the chemical bonding. The Fermi level crosses the lower part of Ce 4f states which are centered above E_F; Ce being an early *RE* element with small occupation of the f subshell. In the mean field Stoner theory of band ferromagnetism [51, 52], this is indicative of stability of the system in such a non-magnetic configuration. The Ru-4d states are centered at -2 eV below E_F. From the similar shapes of the PDOS peaks, the chemical interaction is likely to occur in the [-4 eV to E_F] energy region with the itinerant part of the valence states of the constituents. At lower energies, in the range from -8 to -6 eV, the Al states are found with lower intensity and larger dispersion due to their s,p-like nature. Less bonding will then be expected for them. This is detailed below. Spin-polarized calculations were carried out for a check of the magnetic ground state, and did not lead to the development of an ordered moment on either one of the atomic constituents, especially for Ce at the two crystallographically independent sites.

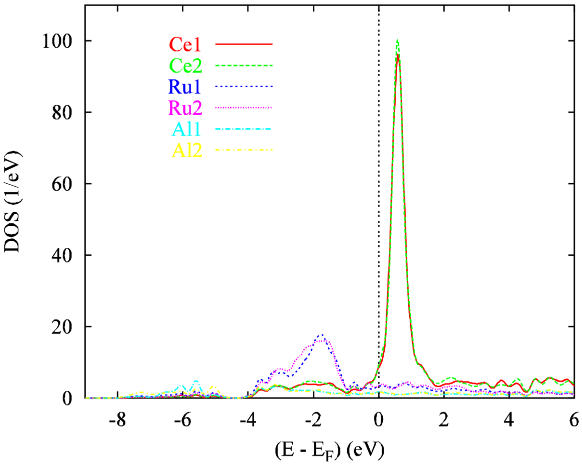


Fig. 3. (color online) Site-projected DOS in CeRuAl (non-spin-polarized configuration).

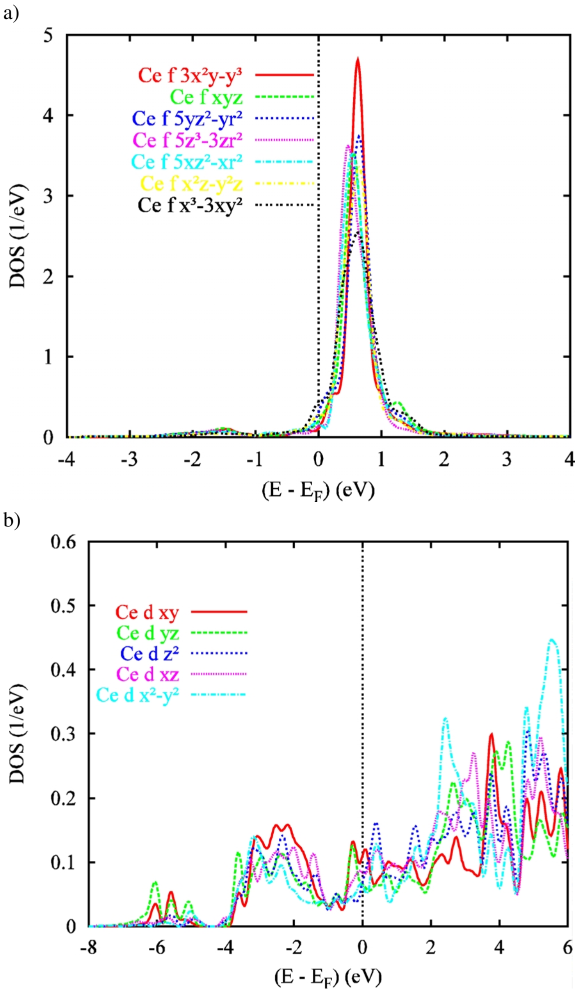
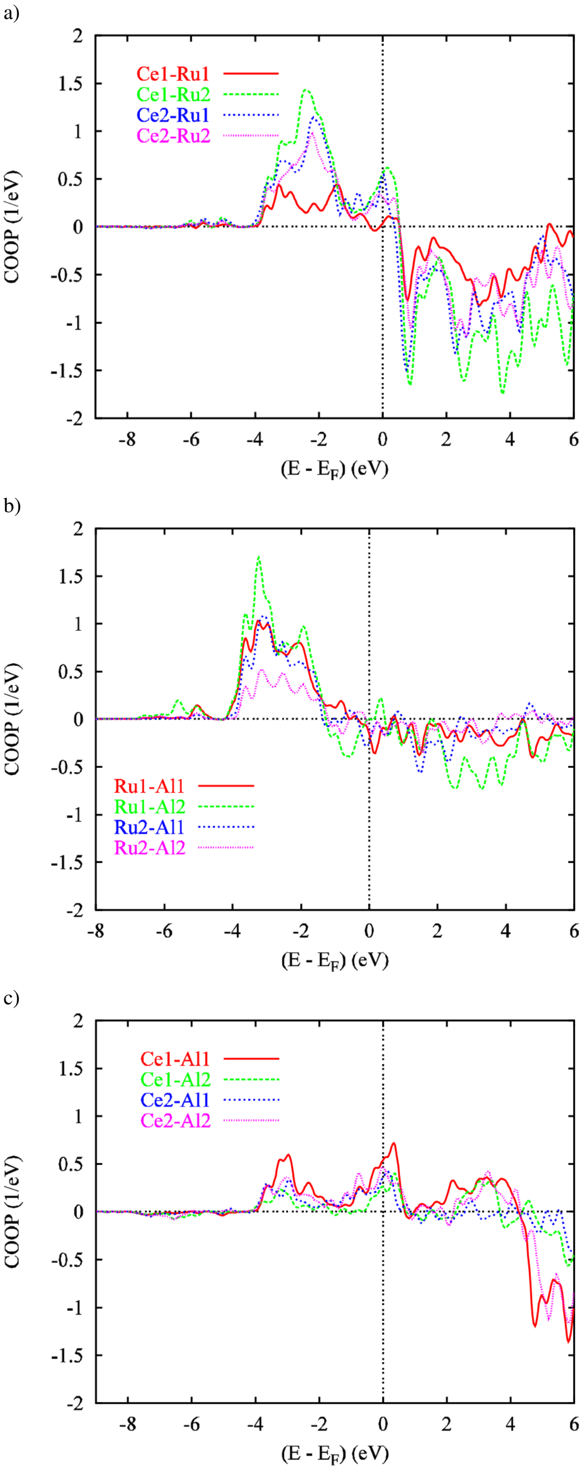


Fig. 4. (color online) Projected f and d orbitals of Ce in CeRuAl (non-spin-polarized configuration).

The participation of the specific orbitals of Ce was addressed by decomposing them over their harmonics. This is shown in Fig. 4 for the 7 f (Fig. 4a) and



⟵ Fig. 5. (color online) Chemical bonding between the different constituents within CeRuAl (non-spin-polarized configuration).

5 *d* orbitals (Fig. 4b); projections for Ce1 are shown here. From the *f*-decomposition, the planar *x*,*y* orbital $3x^2y-y^3$ and x^3-3xy^2 have respectively the largest intensity and the more enhanced density of states at the Fermi level due to the broadening. This is also observed in the much lower-intensity *d* orbitals where d_{xy} shows a slightly larger intensity with respect to the others. Thus it can be suggested that changes in the *x*,*y* plane are likely to play a prevailing role in the bonding and magnetic instability. This bonding is likely to occur through the itinerant Ce *f* and *d* states below E_F on one hand and the valence states of Ru and Al on the other.

The chemical bonding analysis was carried out at a qualitative level based on the COOP criterion, as illustrated in Fig. 5. The plots detail the different interactions between Ce, Ru and Al. The major part of the VB is found to bear a bonding character (positive *y* magnitudes) for the different interactions; the antibonding counterpart (negative *y* magnitude) is found above E_F, in the conduction band. The strongest bonding peak intensity is observed to occur between Ce and Ru on one hand, and between Ru and Al on the other. The Ce–Al COOP's have the lowest intensities. However, the Ce1–Al1 contribution is found to be largest. The involvement of Ce1 states in this bonding weakens its contribution with the other types of bonding. This mainly influences the strength of the Ce1–Ru1 bond which is the smallest one among the Ce–Ru interactions. These are all close in magnitude, but prevail for Ce1–Ru2. For these reasons the strength of the Ce–Ru COOP does not strictly scale with the course of the Ce–Ru distances.

Summing up, CeRuAl is a further example of a cerium compound with short Ce–Ru distances. Susceptibility measurements and electronic structure calculations revealed intermediate cerium valence, a non-magnetic ground state and strong Ce–Ru bonding. Further studies on such Ce-Ru-*X* phases are under way in order to elucidate the interesting structure-property relations of these materials.

Acknowledgements

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