Is Eka-Mercury (Element 112) a Group 12 Metal? *

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The synthesis of the superheavy elements is a challenge for experimental physics that addresses fundamental questions about nuclear structure and stability. [1] Much success has already been made with the synthesis of elements up to $Z = 118$, [2–5] and with the development of real atom-at-a-time chemistry performed on elements up to $Z = 108$, [6, 7] in order to explore the often anomalous behaviour of these esoteric elements. However the detection of such elements relies on a reliable understanding of their chemical and physical properties.

In the case of the trans-actinide elements, starting with rutherfordium ($Z = 104$), experiments have been performed in order to correctly place these elements in the periodic table, or even to address the question of whether the periodic table is still useful for categorising these elements. Due to the very small lifetimes of these elements ($t_{1/2} = 78$s ($^{261}_{104}$Rf) to 14 s ($^{269}_{108}$Hs)), such experiments are highly non-standard and often rely on theoretical predictions for unambiguous interpretation. [8, 9] The latest super-heavy element for which atom-at-a-time chemistry is prepared is element 112 [10, 11] ($t_{1/2}$ for ^{283}112 is 4 s), also known as eka-mercury. The chemistry of element 112 is controversial, as early predictions range from mercury-like [14] to more noble gas like behavior, [8, 15, 16] the latter due to the strong relativistic contraction of the 7s-shell. Hence model studies have already been conducted [10–13] based on the assumed similarity of element 112 to either the noble gas Rn or the transition metal Hg. Predicted data [17] for the elements 112 and 114 were also used to link them to sublimation or adsorption data. Such predictions are of exceptional importance for the design of sophisticated experimental setups for the chemical investigation of transactinide elements on a single atom scale.

The relativistic valence s-contraction is already of fundamental importance for mercury, where for the closed 6s-shell it results in the van der Waals binding of the dimer leading to quite different behaviour for mercury than is observed for zinc and cadmium. For example, mercury is a much poorer metal with a resistivity of 5.8 $\mu\Omega$-cm (at 77 K) compared to zinc and cadmium with 1.1 and 1.6 $\mu\Omega$-cm respectively, [18] and adopts an uncommon rhombohedral structure in the solid. [19] Indeed, it is possible to implicate relativistic effects as responsible for the very low melting temperature of the bulk element. However bulk mercury remains very different to the condensed noble gases. In the case of element 112 these effects can be expected to be further amplified, [20–22] and lead directly to the question of whether element 112 is in fact metallic, or whether it might have more in common with the noble gas solids.

To address the fundamental question of whether, eka-mercury, is metallic in the solid state or not, we performed non-relativistic (NR), scalar relativistic (SR) and four-component relativistic (FR) calculations of the band structure of element 112 (see theoretical section). Since mercury solidifies into a rhombohedral structure distorted from fcc by a change in the rhombohedral angle from 60° to 70°, and yet zinc and cadmium both adopt the hexagonal close-packed (hcp) lattice, we decided to optimise the structure of element 112 in both lattices in the SR case. In the rhombohedral case, we obtain optimised lattice parameters of $a = 3.28$ Å and $\alpha = 61.5^{\circ}$, with a cohesive energy of $E_{coh} = 1.07$ eV. Since this corresponds closely to an fcc lattice, it suggests that the driving force behind the adoption of the 70° angle in mercury is no longer present in element 112. This is reinforced by the results of optimisation in the hcp lattice, where we obtain lattice parameters of $a = 3.34$ Å and $c = 5.36$ Å, with a cohesive energy of $E_{coh} = 1.13$ eV. Reoptimizing the lattice at the FR level of theory only slightly changes the lattice parameters to $a = 3.32$ Å and $c = 5.40$ Å. Thus element 112 prefers the hcp lattice, according to LDA. Curiously the c/a ratio of 1.61 (SR) and 1.63 (FR) is very close to the ideal value of 1.63, which is not the case in zinc and cadmium which have values of $c/a = 1.86$ and 1.89 respectively. Thus element 112 is already at the structural level substantially different from its lighter homologues, and in this sense more closely resembles the rare gas solids. [23] However, the cohesive energy of 112 is slightly larger than that of Hg but one order of magnitude larger than any of the solid rare gases, [23] which resembles closely the behaviour of the dissociation energies of the Group 12 dimers investigated previously. [16] The nearest neighbor distance in solid 112 is 3.30 Å and substantially larger than in rhombohedral mercury of 3.00 Å [24].

In the non-relativistic case we obtain hcp lattice parameters of $a = 3.44$ and $c = 6.06$, with a cohesive energy of $E_{coh} = 1.66$ eV. The increased binding of the NR lattice is an expected consequence of the larger extent of the valence $7s$-shell, and consequently better mixing with the $7p$-shell. The NR lattice is also quite similar to that of zinc and cadmium, with a c/a ratio of 1.76.

The band structures in the SR and NR calculations have both been obtained in the hcp lattice. The NR band structure is comparable to the band structure of zinc and cadmium, where one finds the very flat $6d$-bands well below the Fermi level, and the valence $7s$-band crossing the Fermi level ($E_{Fermi} = -0.17$ eV). The conduction $7p$-band descends to cross the Fermi level near the Γ-point, making the system metallic. The SR band structure is very different, however. The most obvious difference is the appearance of a 0.88 eV band gap, making element 112 an insulator. The $6d$-bands overlap with the $7s$-bands. Due to the overbinding of LDA, we risk some bias towards a metallic structure, which makes the insulating structure found here unlikely to be due to our choice of functional.

In addition we have calculated the band structure at the optimised rhombohedral structure, where we find a slightly smaller band gap of 0.85 eV. This is partly due to the slightly shorter nearest neighbour distance in the rhombohedral structure, 3.28 Å as compared to 3.34 Å in hcp. A NR band structure calculated at the relativistically optimised geometry is also very similar to the NR band structure shown, indicating that the metallicity of the lattice is only weakly dependent on the lattice structure (and then primarily only on the distance parameters).

Due to the neglect of spin-orbit splitting, one cannot exclude the possibility that element 112 becomes metallic as the splitting of the $7p$ level into $7p_{1/2}$ and $7p_{3/2}$ is very large for superheavy elements. [25] Spin-orbit coupling leads to the decrease in energy of the conduction $7p_{1/2}$-band, thereby reducing the size of the band gap. Hence four-component fully-relativistic calculations are essential to answer the question if element 112 is metallic or not, Fig. 1. The band gap is now markedly smaller, only 0.2 eV in this case.

The SR and FR density of states (DOS) for the hcp structure are shown in Fig. 2. Here we see the influence of the spin-orbit splitting clearly; the $6d_{3/2}$ and $6d_{5/2}$ levels are strongly split, by around 3.2 eV, and the two peaks above the band gap may be taken to be the $7p_{1/2}$ and $7p_{3/2}$ levels for which the spin orbit splitting amounts to about 5 eV, from a calculation of the atom-like levels. Due to the relativistic $6d$-expansion and the relativistic $7s$-contraction,the valence bands are of predominantly $6d$-character with a spin-orbit splitting of around 3.2 eV between the $6d_{3/2}$ and $6d_{5/2}$ levels.

We conclude that element 112 is no longer metallic, but a semi-conductor (at normal conditions) with a band gap of at least 0.2 eV as estimated from the LDA, which serves as a lower bound. The band gap is quite small and 112 resembles more closely the Group 12 metals than the rare gases.

Theoretical Section: We performed scalar relativistic (SR) and non-relativistic (NR) band structure calculations using a Stuttgart small-core energy-consistent pseudopotential [21] to model the [Xe]$4f^{14}5d^{10}5f^{14}$ core. [26] From the original optimised valence basis sets diffuse exponents (less than 0.1) were removed, as these lead to linear dependencies and non-convergence of the SCF procedure. The most diffuse remaining functions were reoptimised to a (8s7p5d) set contracted to [7s6p4d]. The cohesive energy is the counterpoise corrected by calculating the atomic energy in the presence of basis functions placed at the positions of neighbouring atoms in the solid. This correction is converged when the first 18 neighbours are used. 133 k-points were used in the irreducible part of the Brillouin zone. The local density approximation (LDA) [27] was used due to its overall good performance for metals, and in particular the rhombohedral structure of solid mercury. [28] We also tested different LDA and GGA functionals as implemented in the CRYSTAL code, none of which gave smaller band gaps (e.g. an increase of the NR band gap to 1.4 eV was obtained with the GGA functional PW91) [29, 30] which supports our interpretation of the LDA value as a lower bound. Additionally, we performed four-component Kohn-Sham-Dirac (FR) band structure calculations at the SR optimised geometry using the relativistic version [31] of the full potential local orbital method [32] (RFPLO). Bloch sums of atom-like local orbitals are used as a basis set. The local orbitals are chosen as solutions of a single particle Dirac equation in the spherically averaged crystal potential and an additional confining potential, which is applied to valence states only. The confining potential contains an orbital dependent variational parameter which is used to adjust the local basis states such that the total energy is minimized. For the present calculations, we used $5f$, $6d$, $7s$ and $7p$ states as basis set. The spin-orbit split $5f$ states form dispersionless bands about 63 and 69 eV below the Fermi energy. The inclusion of $5f$ states in the valence basis only marginally influences the calculated total energy ($\approx 1\mu$Hartree/atom), which justifies *à posteriori* their neglect in the previous geometry optimisations with the CRYSTAL03 code. Including 6f-polarization states leads to negligible changes in the band structure. The site-centered potentials and densities in the calculations were expanded in spherical harmonic contributions up to $l_{max} = 12$. The number of k-points in the irreducible part of the Brillouin zone was 133. The LDA parameterization of Perdew and Wang [33] for the exchange-correlation potential was used. The SR band gap obtained with RFPLO is somewhat smaller than in the CRYSTAL calculation, 0.7 eV compared to 0.9 eV. This variation is not due to the different parametrisation of the LDA functional: The band gap in the CRYSTAL calculation remains unchanged if we employ the PW92 functional, indicating that a difference of around 0.2 eV may be due to the difference between the RFPLO and CRYSTAL codes. A possible source for this difference could be alternative definitions of the SR approximation and basis sets used in both codes.

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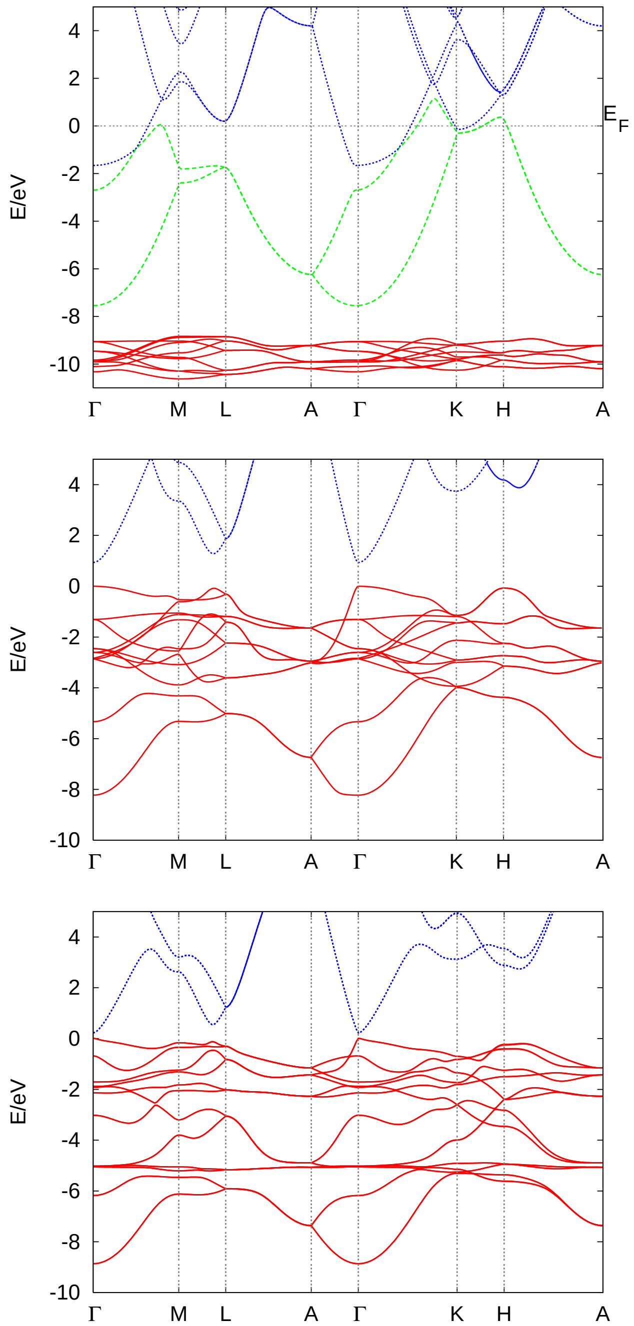

Figure 1: Non-relativistic (top), scalar-relativistic (middle), and fully-relativistic (bottom) band structures for element 112 calculated within the hcp lattice at the LDA optimised geometry. The d-bands are shown in solid red lines, the s-bands are in dashed green lines, and the unoccupied (or conduction) p-bands are in dotted blue lands. (In the relativistic cases there is considerable mixing between the s and d-bands, clearly visible in the DOS, and therefore the strongly mixed s- and d-bands are in solid red lines.) The Fermi energy (or highest occupied level) is set to zero.

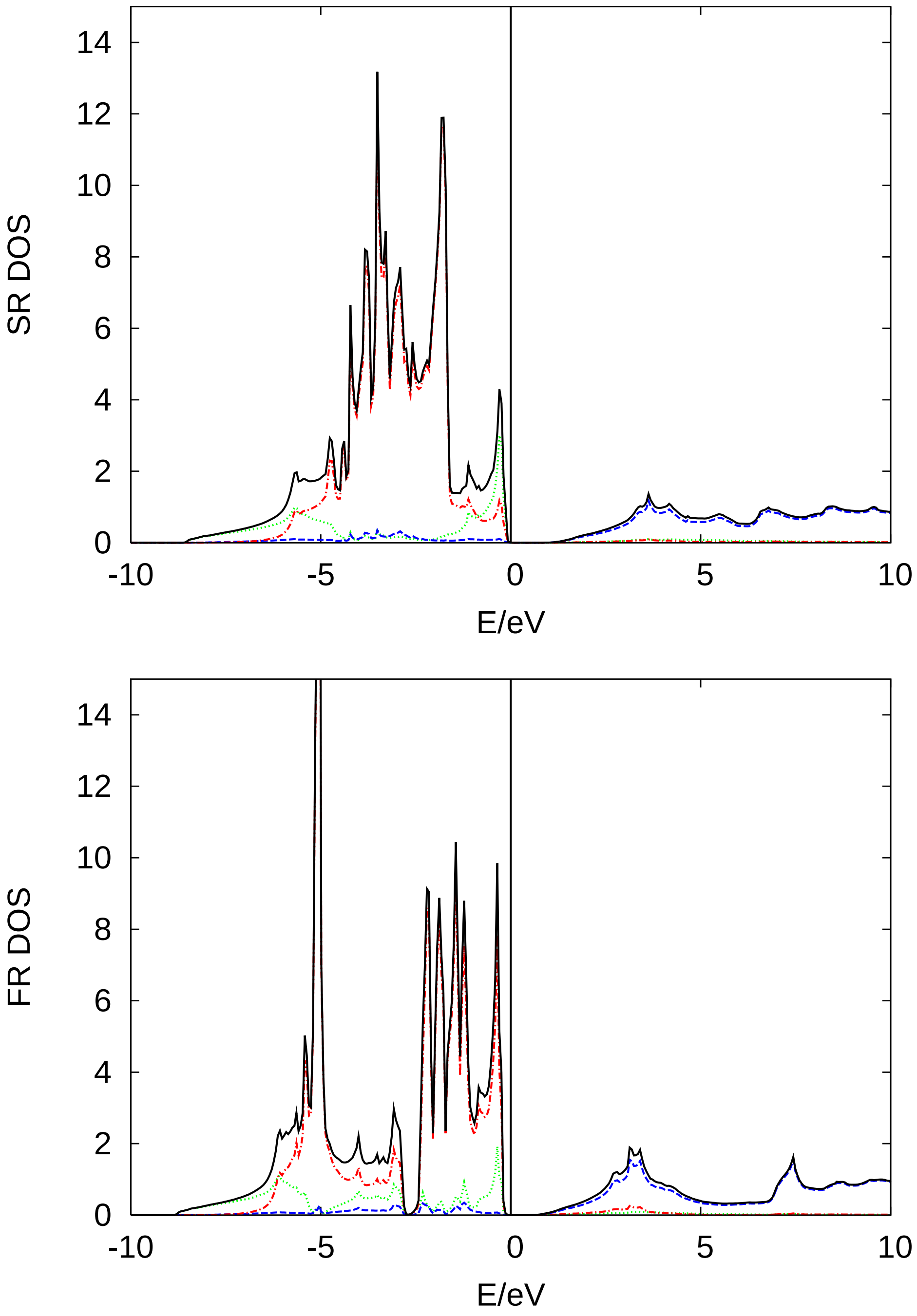

Figure 2: Fully relativistic density of states for element 112 calculated within the hcp lattice at the LDA optimised geometry, and compared to the scalar relativistic DOS in order to see the effect of spin-orbit coupling. The s-bands are in dotted green lines, the p-bands are in dashed blue lines, and the d-bands are shown in dot-dashed red lines. The total DOS is in solid black lines. The Fermi energy (or highest occupied level) is set to zero.

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Super-heavy element 112 is a semiconductor as Dirac-Kohn-Sham band structure calculations show. Non-relativistic eka-mercury would be an hcp metal similar to zinc and cadmium, while the scalar relativistic calculations (neglecting spin-orbit coupling) opens a wide band gap thus becoming an insulator.