Multiple minima on the energy landscape of elemental zinc - a wavefunction based ab-initio study

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Zinc crystallises in the hcp structure, but with an anomalously large c/a ratio, indicating a strong distortion away from ideal packing. Coupled cluster calculations within the frame work of the method of increments, improved by an embedding scheme for metals, were performed to explore the potential energy surface of zinc with respect to the hexagonal lattice parameters. The inclusion of the filled d-shell in the correlation treatment proved to be essential. From the exceptional shape of the potential energy surface the existance of a zinc modification with a nearly ideal c/a ratio can be deduced.

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As a rule, the hexagonally close-packed (hcp) elemental metals, even including high-pressure phases, do not deviate from the ideal ratio of the lattice constants (c/a = 1.63) of this structure type by more than 4%. Zn, Cd and the high pressure modification of Hg [1], however, constitute conspicuous exceptions, showing extreme values of c/a = 1.86 and 1.89 for Zn and Cd respectively, deviating by 14 and 16% from the ideal value. This corresponds to a partitioning of the ideally equal distances for the 12 nearest neighbors into two subsets with 6 by 10% shorter in-plane contacts compared to each three above and below the plane (Fig. 1). This pronounced anomaly can only originate from the electronic structures of the respective elements, since any other constraints that might induce such a distortion are absent. As the reasons for the exceptional packing are not understood so far, investigations with highly accurate computational methods are required in order to analyze the electronic interactions in detail.

In experimental high pressure studies addressing the anomalous c/a ratio in Zn and Cd, irregularities in the pressure dependence of the lattice parameters have been found [2]. A change in the slope of the c/a vs. V/V_0 curve at $c/a = \sqrt{3}$ [1, 3] has been related either to the corresponding special symmetry of the hcp structure both in real and reciprocal space or to a change of the Fermi surface, an electronic topological transition (ETT), which was also discussed in connection with an abrupt change of the Lamb-Mössbauer factor under pressure [4, 5]. The anomalous response of the c/a ratio upon pressure, however, could not be verified experimentally when a different pressure medium was employed [6]. Likewise theoretical studies within the framework of density functional theory (DFT) did not provide an unequivocal picture of the c/a anomaly and its relation to an ETT, as the re-
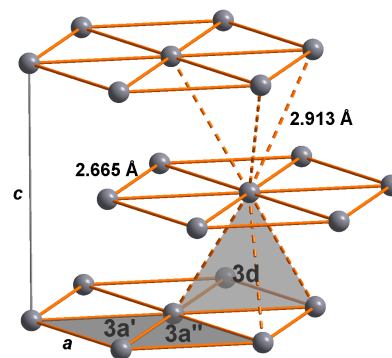

FIG. 1: In the anisotropic hcp form known experimentally for zinc the bonds between planes (dashed) are 10% longer than the bonds within the close-packed planes, leading to an enlarged ratio of the lattice parameters c/a. The grey triangles represent the most dominant 3-body correlation terms as discussed in the text.

sults depend on the functionals and the computational parameters used [7, 8, 9, 10, 11].

Up to now the best agreement between experimental ground state properties like cohesive energy, lattice constants and bulk modulus and the corresponding DFT results were obtained with the PBE functional [12].

However in a recent survey [13] we have shown that the anisotropy of the bonding in Zn, as reflected by the elastic constants, is not described in a well-balanced manner even with this functional. Indeed, the elastic constants related to distortions in the a-b-plane are reproduced better with hybrid functionals with Hartree-Fock and DFT exchange mixed. The drawback of these latter functionals is a worse description of the interlayer interaction,

leading with B3LYP [14] even to a shift of the c value by 0.79 Å or 16% compared to the experiment.

The potential energy surface of Zn with respect to the lattice constants ($PES(a,c)$) turned out to be very flat along a path that corresponds to uniaxial stress along the c axis [13]. Depending on the basis set a second minimum at a nearly ideal c/a (1.56) appears. In this case the barrier is less than 0.02 eV above the minimum near the experimental structure. The topology of the Fermi surface is different at both minima. With the nearly ideal structure it resembles that of Mg. Whether the ETT is the driving force for Zn to adopt the experimental structure is, however, questionable because of the low energy difference.

Another question raised in Ref. 13 is connected to the role of the filled d-shell in the the intra- and inter-layer interactions. Arguments focussing on the hybridisation of the s and p valence bands [15] seem to be not sufficient to describe the deviation from the ideal hcp structure.

In order to analyze different effects on the anisotropic bonding properties in Zn in more detail, the application of wavefunction based methods is necessary. This has some computational cost, but the important advantage that we can systematically judge the perfomance of our calculations. As has been shown in previous studies [16, 17, 18] we believe that an accurate treatment of electron correlation is the key to a correct description of the underlying physics. Highly accurate methods such as coupled cluster techniques can be used for periodic systems within the framework of the method of increments [19, 20].

A many-body expansion of the correlation energy of the solid in terms of local entities allows us to write that $E^{\mathrm{tot}} = E^{\mathrm{HF}} + E^{\mathrm{corr}}$, where the Hartree-Fock energy E^{HF} may be calculated for the periodic system in the standard way, and the E^{corr} may be calculated within the incremental expansion

$$E^{\mathrm{corr}} = \sum_i \epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \ldots$$

The summation over i includes all orbitals in the reference cell, while j and k extend over the entire system. In terms of the correlations considered, the one-body increment involves all excitations from the orbitals i located within the reference cell, while the two-body increment includes the non-additive excitations summed over orbitals i and j; that is $\Delta\epsilon_{ij} = \epsilon_{ij} - (\epsilon_i + \epsilon_j)$. Similarly the three-body contributions may be written as $\Delta\epsilon_{ijk} = \epsilon_{ijk} - (\Delta\epsilon_{ij} + \Delta\epsilon_{jk} + \Delta\epsilon_{ki}) - (\epsilon_i + \epsilon_j + \epsilon_k)$. In the limit of an infinite sum over i, j, k as well as over orders of increments, one would obtain the exact correlation energy per unit cell of the infinite system. Due to the local nature of correlation, the incremental expansion converges swiftly with distance, although the exact convergence behaviour must be tested for any real system.

The neglect of four-body and higher terms is possible even in metals if a carefully designed embedding scheme is applied [21]. Moreover, this provides a physical environment that does not exhibit surface charging of finite metal clusters, and has a disappearing band gap even at small sizes.

In order to be able to investigate a wider area of the potential energy surface with respect to the hexagonal lattice parameters, $PES(a,c)$, a compromise had to be found between computational expense and accuracy by further limiting the number of two- and three-body terms in the incremental expansion. We include the first 7 two-body increments (up to a distance of $2a$ in the experimental structure) and the first 10 three-body increments that have one bond at the nearest or second nearest neighbour distance and a maximum bond length of $2a$. This turned out to be a balanced choice of intra- and inter-layer increments, as well as of positive and negative 3-body terms [22]. At each point of the $PES(a,c)$ we consistently include the same increments as ordered at the experimental lattice structure, rather than reordering the increments. This topological approach is important because the sign of the contribution of the three-body terms depends on the angle, and thus a strict distance cutoff to truncate the sum over three-body terms would introduce small discontinuities in the total energy.

The Hartree-Fock energy was evaluated by periodic mean-field calculations using the program package CRYSTAL06 [23]. The chemically inactive [Ne] core of the Zn atom was simulated by an energy-consistent scalar-relativistic pseudopotential [24]. The basis sets used are contracted Gaussian type orbital (CGTO) sets obtained from the Dunning-type cc-p-vTZ basis sets [25], optimised for the 20-valence electron pseudopotential [24] and modified [22] to meet the requirements of the CRYSTAL code. We performed a counterpoise correction using 24 neighbours in the solid to correct the crystal basis set for the atomic energy at any point of the potential energy surface.

The incremental correlation energies were computed with the coupled cluster code as implemented in MOLPRO [26] with single, double and perturbative triple excitations (CCSD(T)) [27, 28], using the aug-cc-p-vTZ basis set with additional decontraction of the exponents [25]. Separate calculations with and without inclusion of the d-orbitals in the coupled cluster treatment allow for an investigation of the influence of the filled d-shell on the correlation energy and thus on the bonding properties.

The contributions of HF and of the 1-body, 2-body and 3-body terms to the binding energy are represented separately in Fig. 2. At the HF level zinc is not bound, being expressed by a positive binding energy of 0.09 eV, at the experimental lattice parameters. As is natural for a purely repulsive potential this value increases with decreasing distance (Fig. 2a). The negative gradient points to smaller c/a ratios.
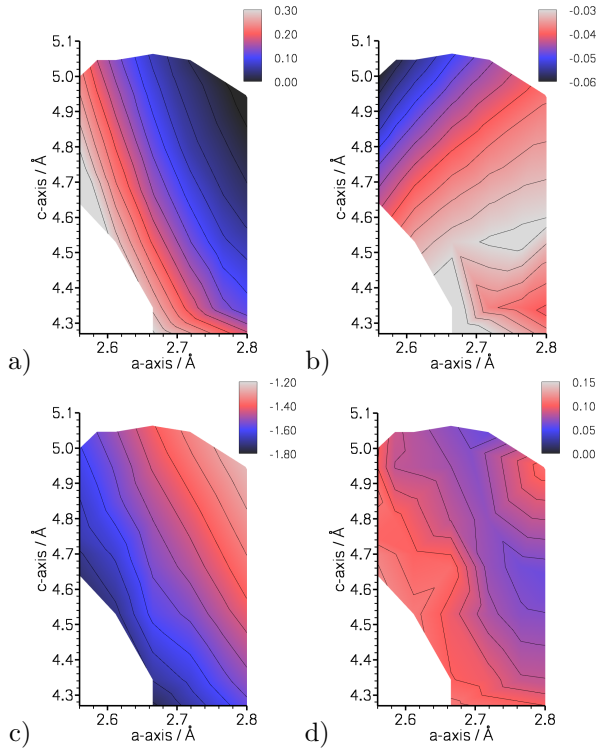
FIG. 2: Contributions to the binding energy of Zn in eV: a) HF; b) 1-body increments; c) 2-body increments; d) 3-body increments. The increments include d-correlation. Note the different scales of the contour plots.

The positive 1-body terms of the valence shell are cancelled out after including the d-shell in the correlation treatment, leading to rather low negative contributions (Fig. 2b). The by far largest part of the correlation energy is due to 2-body increments. Within the area of the PES(a,c) regarded here, this contribution to the binding energy increases monotonically with decreasing lattice constants (Fig. 2c). The gradient is not closely parallel to lines of constant c/a, favouring larger c/a ratios. When omitting the d-correlation the monotonic shape remains the same, but the absolute values are 23 % smaller and, moreover, the gradient is smaller by more than a factor of two. Thus, without d-correlation, the repulsive HF potential cannot be compensated adequately, leading to a considerably larger a-parameter (Fig. 3b). In this case no minimum is found at the experimental lattive constants, and the binding energy is only -0.8 eV.

Compared to the monotonic behaviour of the other terms, the 3-body contributions depend in a complex manner on the lattice constants (Fig. 2d). In the whole area the 3-body values are positive. They are higher at low a- and c-parameters, partially balancing the attractive nature of the 2-body terms. The most dominant individual 3-body increments are coming from the smallest triangles in the lattice, in-plane, denoted 3a' and 3a" in Fig. 1, and out-of-plane, denoted 3d. (Although 3a' and
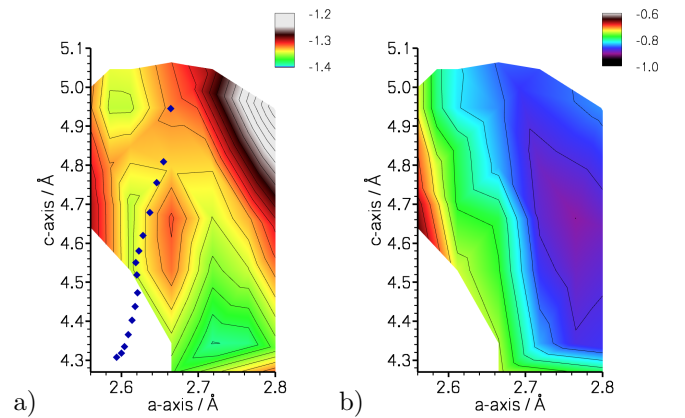

FIG. 3: Total binding energy of Zn with respect to the lattice constants (in eV), with (a) and without (b) d-correlation. Note the different scales of the contour plots. The blue diamonds in the left diagram mark the lattice constants measured by Takemura [1] under high pressure.

3a" are based on an equivalent correlated cluster, they vary due to different crystallographic positions and thus due to different embedding.) All three increments are positive and the repulsion increases with shrinking lattice constants. An increase of the in-plane terms, forced by the highly attractive 2-body contributions, however, can be compensated by a decrease of the out-of-plane term at a larger c-parameter. The compensation is one of the reasons for the anisotropic crystal structure of zinc.

The PES including valence- and d-correlation is presented in Fig. 3a. The cohesive energy at the minimum called 'expt-like' in Tab. I matches the experimental one. The corresponding a-parameter deviates by -2%, the c-parameter by less than 1%. One reason for the overbinding in the a-b-plane may be the neglect of the correlation contributions of the semi-core orbitals (3s,3p). They were computed for a few points on the PES and lead to a reduction of the binding energy by 0.01 to 0.02 eV. The effect is smaller at larger lattice constants.

In contrast to other elements like Mg [18], Zn has a much more complex energy landscape. Behind a barrier of 0.02 eV height towards smaller c-parameters it features two valleys separated by a ridge. The corresponding minima are called 'ideal-like' and 'min-3' in Tab. I. This exceptional shape is the consequence of the complex interplay of the 3-body terms as discussed above. The 'ideal-like' minimum with a nearly ideal c/a ratio even exhibits a slightly larger binding energy than the 'expt-like' one. This fact raises the question why the 'ideal-like' minimum thus far has not been accessible via high pressure experiments. The reason is given by the special shape of the energy landscape. Due to the hydrostatic conditions in the experiments that prevent a significant expansion of the a-b-plane, the system moves through the left valley. Taking into account that our calculations

TABLE I: Lattice constants (Å), cohesive energies (eV) and cell volumes (Å^3) for minima on the potential energy surface PES(a,c) of zinc.

		a	c	c/a	E_{coh}	V
expt [a]		2.67	4.95	1.86	-1.35	30.4
this work	expt-like	2.61	4.98	1.91	-1.35	29.3
	ideal-like[b]	2.72	4.34	1.60	-1.39	27.8
	min-3[b]	2.61	4.70	1.80	-1.35	27.7
GGA(PBE) [13]	expt-like	2.65	5.12	1.93	-1.00	31.1
	ideal-like	2.82	4.40	1.56	-0.99	30.3

[a]Lattice constants [29], cohesive energy [30]
[b]Data points in the computed grid with high binding energy

slightly overestimate the binding in the hexagonal plane, the high pressure data of Takemura [1] fit very well to our PES (Fig. 3a). The additional local minimum in the left valley ('min-3' in Tab. I) is another indication for the strong bond in the hexagonal planes and may further explain the anomalies observed in high pressure experiments under certain conditions.

Using the methods of increments we have been able to draw a detailed picture of the hcp structure of zinc. Besides the analysis of the PES and its relation to experimental data, mechanisms for the anisotropy are worked out, that lead to a layered structure. We emphasize the necessity of including the filled d-shell in the treatment of the electronic correlation. The existence of a zinc modification with a nearly ideal c/a ratio is possible.

Acknowledgements

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