Ab initio correlation calculations for the lattice structures of Zn, Cd, and Hg

Nicola Gaston[1] and Beate Paulus

Max-Planck-Institut für Physik komplexer Systeme,
Nöthnitzer Straße 38,
01187 Dresden, Germany

Abstract: Mercury condenses at 233 K into the rhombohedral structure with a bond length $a = 3.005$ Å and an angle of 70.53º. In contrast, zinc and cadmium adopt the hexagonal close-packed (hcp) structure, but with an anomolous c/a ratio which is far from ideal hcp. Density functional methods fail to describe either of these structures accurately. An application of the method of increments to these metals, including correlation via coupled cluster calculations on finite fragments of the solid, allows the systematic inclusion and comparison of the competing effects that leads to the observed structures.

Keywords: Ab-initio calculation; Electron correlations; Method of increments; Relativistic effects

PACS: 61.50.Ah, 61.50.Lt, 62.20.Dc

1 Introduction

The anisotropic lattice structures of Zn, Cd and Hg are well known. However a clear description of the origin of this effect, and its different manifestations in either the hexagonal-close-packed (hcp) structure (for Zn and Cd) or the rhombohedral structure (Hg), remains challenging. The zinc and cadmium lattices are hcp, but not ideal as there are only 6 nearest neighbours at a_0 instead of 12. These are in the hexagonal plane, while the next 6 neighbours are at a significantly longer distance a_1 above and below the plane. Thus this distortion corresponds to an elongation of the c-axis, which increases going from zinc to cadmium. In the rhombohedral structure of mercury, while there are also 6 neighbours at a_0 and 6 neighbours at a_1, the nearest neighbours (at a_0) form a distorted octohedron (with angles 70.5º instead of 90º) instead of lying in the plane. The ideal hcp structure is, as the name suggests, close-packed, which requires that the ratio of the two lattice parameters be $c/a = \sqrt{8/3}$. This is indeed the case for a metal such as magnesium, which differs from zinc only in the absence of the 3d-shell. Therefore the anisotropic ratios in Zn and Cd ($c/a = 1.86$ and 1.89 respectively), which indicate a layered structure with strongly bound hexagonal planes that are only weakly stacked, must be due to the presence of the d-shell. However in the case of Hg, the same anisotropy manifests itself in the adoption of a rhombohedral structure (for 79 K < T < 234 K), which is unusual for an simple metal. Thus the question of how the structures of these metals are related depends on an understanding of the influence of relativistic effects on the d-shell. A summary of the trends observed in various properties of Zn, Cd, and Hg (particularly the solid) is given in Tab. 1.

---

[1]Corresponding author. E-mail: ngaston@pks.mpg.de

	Zn	Cd	Hg	Ref.
r_e (dimer) /Å	4.19	4.07	3.69	[2, 3]
a_0 (solid) /Å	2.66	2.98	2.99	[4]
crystal type	hcp	hcp	rhomb	
a_1/a_0	1.09	1.12	1.15	
c/a (expt)	1.86	1.89		[4]
c/a (hcp-lda)	1.91	1.78	1.41	[5, 6]
Resistivity (77K) /μohm-cm	1.1	1.6	5.8	[4]
N (band-gap closing in clusters)	$\sim$18		$\sim$400	[7, 8]
Melting T /K	693	594	234	[4]

Table 1: A comparison of important properties of the Group IIB metals. In the case of Hg, there exists no ratio c/a (expt), therefore the lda optimised value of c/a in the hcp structure is also given, for comparison.

The importance of relativistic effects in the mercury atom is well known and understood, and can often be related to the difference in the properties of solid Zn and Cd compared to Hg. For example the smaller band gap seen in Hg clusters than in Zn clusters, and the consequently later onset of metallic behaviour, is clearly due to the strong relativistic contraction of the valence 6s-shell. However the issue of the rhombohedral lattice structure of Hg is more complicated, requiring a closer analysis of the different effects that contribute to this distortion. One clue is provided by the value of c/a in solid mercury. There is no tabulated experimental value of c/a for mercury. An optimisation of the hcp lattice for Hg, performed with LDA which is the only density functional to find the rhombohedral structure as the minimum and therefore describe mercury approximately correctly (see [6]), finds an optimum value of $c/a = 1.41$. This would correspond to a structure with weakly bound hexagonal planes with strong binding between layers. However in a recent study of the high pressure structures of Zn and Cd [1], it has been speculated that there exists a lower bound to the stability of the hcp structure, with an axial ratio $c/a = 1.50$, as there is a special symmetry that develops at this point both in real and reciprocal spaces. The $\Gamma\Gamma$, ΓL, and ΓK distances become degenerate, leading to the formation of regular hexagons in planes perpendicular to the ΓK directions. This may explain the structural transformation from a no longer stable hcp lattice to the rhombohedral structure of mercury, however we can hardly take the LDA evidence as conclusive when it performs relatively badly for Zn and Cd.

Density-functional theory (DFT, see [9, 10]) is currently the usual method for studies of infinite systems. The use of reasonable approximations such as the local density approximation, LDA, or generalized gradient approximations, GGA, give reliable results for a wide variety of systems. However in the case of the group IIB metals, DFT is quite unsuccessful. For mercury LDA provides qualitatively and quantitatively reasonable results, although the agreement may be to some extent fortuitous, due to the normal overbinding behaviour of LDA. All other functionals find a cubic (fcc) structure to be more stable [6]. For Zn and Cd an LDA description is quite erroneous, and the PBE functional performs best, although such an ad-hoc choice of functional is wholly unsatisfactory. No single such approximation can be considered to perform best in a systematic way, and there is no systematic way in which DFT can be improved. The use of *ab initio* correlation methods, such as coupled cluster, is therefore desirable. As currently the application of such highly accurate

methods to infinite systems is not directly possible, we study the correlation effects in the solid in a systematic way via the method of increments.

2 The method of increments for metals

As described in Ref. [11], we include electronic correlation in a procedure known as the method of increments. A review of this approach describes its application to systems including van der Waals (vdW) solids, insulators and metals [12]. A general many-body expansion for the correlation energy may be written in the form

$$E_{corr} = \sum_i \epsilon_i + \sum_{i<j} \Delta\epsilon_{ij} + \sum_{i<j<k} \Delta\epsilon_{ijk} + \dots \quad . \tag{1}$$

Such an expansion, where the n-body indices $i, j, k, \dots$ number individual atoms, is known to work extremely well for vdW crystals. For noble gases [13, 14] it is even possible to include the Hartree-Fock (HF) part of the energy within the many-body expansion, and already a two-body potential (e.g. in the form of a Lennard-Jones potential) gives quite reasonable results. However, for mercury an expansion of the total energy converges only slowly [15]. This is due to the changing character of the Hg-Hg bond in mercury, which for the dimer is indeed vdW-like, but becomes progressively more covalent as the number of atoms increases and metallic in the case of the bulk [16]. The contraction of the bond between the dimer and the bulk is even more pronounced for zinc and cadmium, ($\sim$1.5 Å for zinc), and therefore such an expansion of the correlation energy only is also suitable. However the nature of the 3-body contribution is markedly different in zinc and cadmium than what we have seen in mercury.

The HF energy is calculated with CRYSTAL [17], and corrected for the basis set superposition error (BSSE) by a counterpoise correction with the atomic energy calculated in the presence of basis sets placed at the positions of neighbouring atoms in the solid (convergence required 12 nearest neighbours for Hg, 18 for Zn and Cd). We calculated the correlation energy of the 1-, 2-, and 3-body increments in clusters which are really frozen fragments of the solid. The atoms to be correlated are surrounded by an embedding which is defined by a cutoff distance ($1.7a_0$). These atoms are described by Stuttgart small core relativistic pseudopotentials with the corresponding valence aug-TZ basis set. (See Ref. [18, 19, 20] for details). The embedding atoms are described by large core pseudopotentials with a minimal s-basis set only. The correlation energy is calculated with the coupled cluster method including single, double and perturbative triple excitations (CCSD(T)) as implemented in the program Molpro [21]. For the 2-body increments, we include all pairs up to the distance $2a_0$, and for the 3-body increments, we take the first 9 triples ordered by increasing average bond length.

The energy decomposition into HF and 1- and 2-body correlation contributions is shown for Zn and Hg in Fig. 1. The importance of correlating the underlying d-shell is highlighted by showing separately the curves obtained by correlating only the valence s-shell, and then all electrons. The correlation of the core s- and p-shells is typically 1% of the d- and s-shell correlation, and can be neglected. Only with d-shell correlation do we find a minimum at the 2-body truncation of the method of increments, and for mercury it is only at this level that the solid becomes bound.

The results of the method of increments for Zn, Cd, and Hg for the cohesive energy of the experimental lattice structure are given in Tab. 2, both for the inclusion of all terms up to the 2-body increments and also including 3-body increments.

In the case of Hg, the 3-body contribution is cohesive, as expected, about 30% of the total cohesive energy. In contrast, in Zn and Cd the 3-body contribution is less than 5% of the cohesive energy, and is repulsive. It seems reasonable that this large difference in the behaviour of the 3-body energy is connected to the change of structure from hcp to rhombohedral. Therefore we
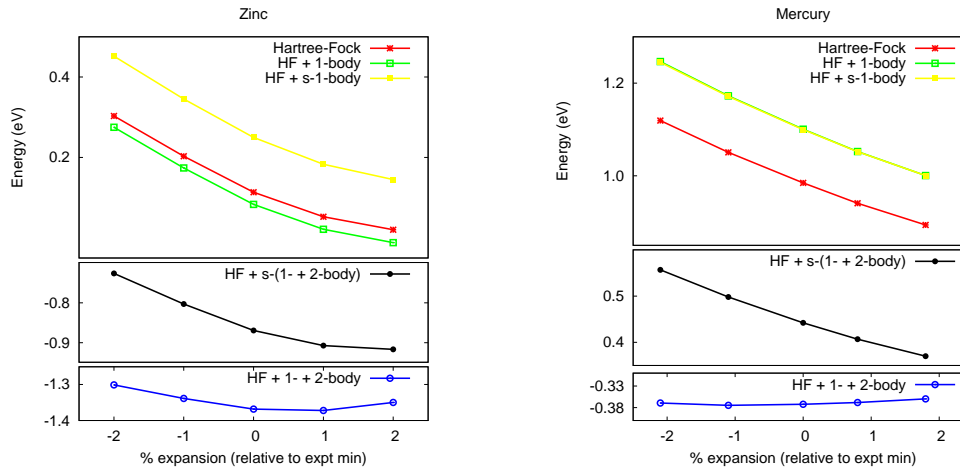
Figure 1: The energy decomposition of the cohesive energy of Zn (left) and Hg (right), according to the method of increments. The x-axis shows the isotropic expansion parameter describing the expansion/contraction of the solid with respect to the experimental structure.

Cohesive Energy	Zn	Cd	Hg
MOI-2	1.368	1.356	0.469
MOI-3	1.310	1.297	0.694
Experiment	1.350	1.160	0.670

Table 2: A comparison of the cohesive energies (eV, at the experimental lattice parameters) calculated with the method of increments (MOI), with up to 2-body or additionally 3-body correlation included (MOI-2 and MOI-3 respectively). The experimental cohesive energy is also given [22].

compare briefly the particular 3-body structure which contributes most strongly to this difference, the compact nearest neighbour trimer which is the equilateral triangle in the case of hcp, and the triangle with two bonds a_0 and one $a_1 = 1.15a_0$ (angles 70.5°,54.7°,54.7°) in the case of mercury. The results are compared in Tab. 3.

In the hcp structure the equilateral eq(a_1, a_1, a_1) has a stronger contribution to the cohesive energy of the solid than eq(a_0, a_0, a_0) due to a higher weighting; the individual (unweighted) contributions are naturally lower in eq(a_1, a_1, a_1) than in the NN-3-body cluster eq(a_0, a_0, a_0). The nearest neighbour 3-body energies indicate the important gain in the cohesive energy of the 3-body contribution available to mercury by adopting the rhombohedral structure, rather than the hcp structure. This is emphasised by the comparison with the equilateral trimer (a_1, a_1, a_1),

Cohesive Energy /meV	Zn	Cd	Hg
NN-3-body	-34.9 (2)	-27.6 (2)	100.8 (6)
eq(a_1, a_1, a_1)	-52.9 (6)	-46.8 (6)	-10.2 (2)

Table 3: A comparison of the cohesive energy (weighted for the contribution to the binding of the solid, weights given in parentheses) of the nearest neighbour 3-body increment (defined as the most compact trimer). The equilateral triangle with 3 second nearest neighbour distances which would also exist in the hcp structure is also given, for comparison. (All calculations at the experimental lattice parameters).

which occurs in both structures. The cohesive contributions of the rhombohedral-type 3-body interactions are maximised, and the repulsive contributions of the hcp-type equilateral triangles are minimised.

3   Conclusion

The method of increments has been applied succesfully to the group IIB metals Zn, Cd, and Hg, and obtains cohesive energies in good agreement with experiment at the experimental lattice parameters. The d-shell correlation energy has been shown to be important both for Zn and Hg, at 40% and 200% of the cohesive energy at the 2-body level for Zn and Hg respectively. The nearest neighbour 3-body interaction of mercury in the rhombohedral structure is strongly cohesive; in the hcp structure it would be repulsive. Therefore we are able to see individual effects that lead to the change of lattice structure from hcp for Zn and Cd to rhombohedral for Hg.

Acknowledgments

References

[1] T. Kenichi, *Physical Review B* **56** 9, 5170-5179 (1997).

[2] M. A. Czajkowski and J. Koperski, *Spectrochimica Acta A*, **55**, 2221–2229, (1999).

[3] J. Koperski, J. B. Atkinson, and L. Krause, *Chemical Physics Letters*, **219**, 161, (1994).

[4] N. W. Ashcroft, and N. D. Mermin. *Solid State Physics*. Brooks-Cole, Cornell University, (1976).

[5] B. Paulus, K. Rosciszewski, P. Sony and U. Wedig, in preparation.

[6] N. Gaston, B. Paulus, K. Rosciszewski, P. Schwerdtfeger and H. Stoll, *submitted to Physical Review B* (2006)

[7] O. Kostko, G. Wrigge, O. Cheshnovsky and B. v. Issendorff, *The Journal of Chemical Physics* **123** 221102 (2005)

[8] R. Busani, M. Folkers, and O. Cheshnovsky. *Physical Review Letters*, **81**, 3836–3839, (1998).

[9] R.M. Dreizler and E.K.U. Gross, *Density Functional Theory*, Springer-Verlag, Berlin (1990)

[10] C. Fiolhais, F. Nogueira, and M. Marques (eds.), *A Primer in Density Functional Theory*, Lecture Notes in Physics, vol. 620, Springer, Berlin, 2003.

[11] B. Paulus, K. Rosciszewski, N. Gaston, P. Schwerdtfeger and H. Stoll, *Physical Review B*, **70**, 165106 (2004).

[12] B. Paulus, *Physics Reports*, **421**, 1 (2006).

[13] K. Rosciszewski, B. Paulus, P. Fulde and H. Stoll, *Physical Review B*, **60**, 7905 (1999).

[14] P. Schwerdtfeger, N. Gaston, R. P. Krawczyk, R. Tonner, and G.E. Moyano, *Physical Review B*, **73**, 064112 (2006).

[15] G.E. Moyano, R. Wesendrup, T. Söhnel and P. Schwerdtfeger, *Phys. Rev. Lett.* **89**, 103401 (2002).

[16] H. Haberland, H. Kornmeier, H. Langosch, M. Oschwald and G. Tanner, *Journal of the Chemical Society. Faraday Transactions*, **86**, 2473 (1990).

[17] V.R. Saunders, R. Dovesi, C. Roetti, et. al. *program Crystal 98*, Theoretical Chemistry Group, University of Torino (1998).

[18] The Stuttgart Pseudopotential Library, H. Stoll, M. Dolg and others, (see http://www.theochem.uni-stuttgart.de/pseudopotentials).

[19] D. Figgen, G. Rauhut, M. Dolg, H. Stoll, *Chemical Physics*, **311**, 227 (2005).

[20] K.A. Peterson, C. Puzzarini, *Theoretical Chemistry Accounts*, **114**, 283 (2005).

[21] MOLPRO version 2002.6 - a package of *ab-initio* programs written by H.-J. Werner and P. J. Knowles and R. Lindh and M. Schütz and others, (see http://www.molpro.net), Birmingham, UK, 2003.

[22] C. Kittel. *Introduction to Solid State Physics.* seventh edition, John Wiley and Sons, New York, Chichester, (1996).