The unusual structure of the mercury chalcogenides: relativistic effects in the solid state

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"While I'm still confused and uncertain, it's on a much higher plane, d'you see, and at least I know I'm bewildered about the really fundamental and important facts of the universe."

Terry Pratchett, Equal Rites

Abstract

Mercury oxide in its solid state crystallizes in a rather unusual structure and at ambient pressure two equally intriguing yet different polymorphs are distinguished. Both the low-temperature so-called montroydite form and the high-temperature cinnabar modification consist of planar O-Hg-O zigzag or spiral chains. These sophisticated structures significantly differ from those found for the lighter group 12 chalcogenides zinc oxide and cadmium oxide, which under ambient conditions are known to crystallize in rather simple hexagonal wurtzite and cubic rocksalt or zinc blende structures. Descending the chalcogenide group in the periodic table, the cinnabar structure disappears as an equilibrium modification for mercury selenide and telluride but is still present as a high-pressure modification. However, the deviations in the crystal arrangement between the mercury chalcogenides as opposed to the corresponding zinc and cadmium congeners are still obvious in terms of a different coordination.

Considering this curious behaviour of the mercury chalcogenides the question arises: What causes the occurrence of the unusual structures in the mercury chalcogenides? To this end relativistic as well as nonrelativistic density functional calculations have been carried out to investigate this question with respect to the influence of relativistic effects. Even though relativistic effects in atoms and molecules are well-known and understood, little attention has been given to their influence on the electronic structure and properties of the solid state yet.

The study at hand for the first time demonstrates that the structural differences between the mercury chalcogenides and their lighter zinc and cadmium congeners are a result of relativistic effects. The montroydite and cinnabar modifications of HgO and HgS disappear if relativity is neglected due to a substantial decrease of the cohesive energies by up to 2.2 eV. This deviation becomes smaller for HgSe and HgTe, yet a slight change in the coordination can be attributed to the influence of relativity. Furthermore, the electronic structure and density of states of the mercury chalcogenides are discussed with respect to relativistic effects including the consideration of spin-orbit effects. It was found that relativistic effects have a major impact on the electronic structure. In mercury selenide and telluride the neglect of relativity goes as far as changing the experimentally observed semimetallic behaviour to the restoration of semiconducting properties.

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Nomenclature

ADA   Averaged Density Approximation

ADX   Angle Dispersive Xray

AIMD   Ab-Initio Molecular Dynamics

APW+lo   Augmented Plane-Wave method plus Local Orbitals

CBM   Conduction-Band Minimum

CC   Coupled Cluster

CI   Configuration Interaction

DFT   Density Functional Theory

DOS   Density Of States

EDX   Energy Dispersive Xray

EOS   Equation Of State

EXAFS   Extended X-ray Absorption Fine Structure

FFT   Fast-Fourier Transform

FP   Full Potential

GDSP   Gaussian Dual Space Pseudopotentials

GGA   Generalized Gradient Approximation

GTO   Gaussian Type Orbital

HF   Hartree-Fock

IBZ   Irreducible Brillouin Zone

LAPW   Linearised Augmented-Plane Wave

LCAO   Linear Combination of Atomic Orbitals

LDA   Local Density Approximation

LMTO   Linear Muffin-Tin Orbital

LSDA   Local Spin-Density Approximation

MBPT   Many-Body Perturbation Theory

MD   Molecular Dynamics

MP2   2nd order Møller-Plesset pertubation theory

MR   Multi Reference

NAO+GC   Natural Atomic Orbital plus Gradient Corrections

PBE   Perdew-Burke-Ernzerhof functional

PP   PseudoPotential

PW   Plane Wave

PW91   PerdewWang 1991 functional

SCF   Self-Consistent Field

SCR   Self-Consistent Relativistic

TB   Tight Binding

US   UltraSoft pseudopotential

VASP   Vienna Ab-initio Simulation Package

VBM   Valence-Band Maximum