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**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 perturbation 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