

Solid State Density Functional Calculations for the Group 11 Monohalides

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The group 11 monohalides are characterized by a variety of different solid-state structures and modifications. The copper halides crystallize mainly in a cubic zinc blende structure, while silver halides are mostly found in a rock salt modification. Completely different are the gold compounds where relativistic effects change the symmetry from a cubic to a chainlike AuX arrangement (X = F, Cl, Br, I) with short Au–Au internuclear distances. Here we present a systematic study of all solid state group 11 halides by scalar relativistic density functional theory for the experimentally known and observed structures, as well as for other unknown modifications and compare their relative stability.

Introduction

The understanding of the solid-state structures of group 11 halides is beside other binary AB systems of particular interest as a variety of different modifications and interesting structures can be found. At ambient conditions the copper(I) halides CuCl(s) (nantokite), CuBr(s), and CuI(s) (marshite) crystallize in a 4-fold coordinated zinc blende structure (Figure 1A). The fluoride CuF(s) is unknown (despite a few claims) as it easily disproportionates into CuF₂(s) and solid copper, while in the gas phase the decomposition of CuF₂ into CuF is observed.¹ From further experimental proof CuCl and CuBr undergo phase transitions under high hydrostatic pressure from the more stable 4-fold zinc blende to a 6-fold rock salt coordination.² These transitions to the rock salt structure occur at ~10 GPa via several intermediate phases of apparently lower symmetry, but according to experiment they all retain a tetrahedral Cu⁺ coordination.²

In contrast to copper, the silver halides AgF, AgCl, and AgBr all crystallize at room temperature and low pressures in the simple cubic rock salt structure (Figure 1B). For AgI, three modifications are found at low pressures, i.e., a cubic zinc blende modification (γ -AgI, miersite), a hexagonal wurzite modification (β -AgI, iodargyrite), and a cubic high-temperature modification (α -AgI), which incorporates a molten-silver substructure. At higher pressures all silver(I) halides (AgF, AgCl, AgBr, and AgI) transform according to studies of Hull et al.³ and others^{4,5} from a 6-fold coordination via several intermediate (rock salt related) phases to higher 8-fold CsCl-type coordination spheres, although there has been some discussions on the nature of these phase transitions.⁶ While for AgF this transition is relatively abrupt and occurs at moderate pressures around 2.70(2) GPa,^{4,7} the phase transitions are more complex for the other halides. Monoclinic KOH-like and orthorhombic TII-type structures can be found in between, and much higher pressures (>10 GPa) are needed for the 8-fold coordination (CsCl).³

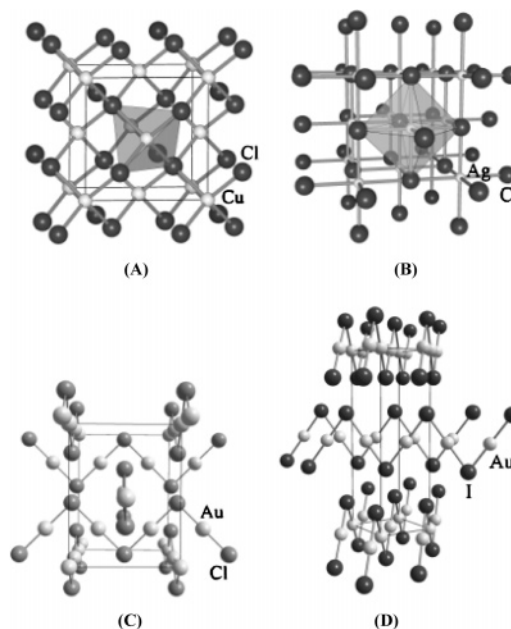


Figure 1. Zinc blende structure of CuCl (A), rock salt structure of AgCl (B), and the chainlike tetragonal structures of AuCl, chain-I (C), and AuI, chain-P (D).

Finally, the most interesting situation is found for the gold halides. They crystallize in unexpected chainlike tetragonal structures (Figure 1, parts C and D), which cannot be so easily rationalized by simple electrostatic or ionic arguments used for the CuX or AgX structures.⁸ As it is obvious from Figure 1, parts C and D, the gold halide modifications show linear AuX₂ units with short Au–Au distances that have been ascribed to aurophilic interactions. There are two alternative but equally valid explanations for these unusual structures depending if electron correlation⁹ or relativistic effects¹⁰ are discussed. At the relativistic Hartree–Fock level (neglecting electron correlation), the cubic and chainlike structures are nearly degenerate and electron correlation stabilizes the chainlike structures.⁹ Alternatively, at the nonrelativistic correlated level the cubic structures are clearly favored and relativity stabilizes the

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TABLE 1: Small Basis Set (SB). B3LYP Optimized Exponents for the (Valence) Basis Functions for the Metals M (M = Cu, Ag, Au, Au (NR) and the Halogens X (X = F, Cl, Br, I)^a

functions	Cu	Ag	Au	Au (NR)	F ^b	Cl	Br	I
s	53.672314	9.104399	13.147170	11.216052	587.954756	12.608534	4.471178	2.147815
	9.555646	7.192119	11.416166	8.511476	102.358092	2.338583	2.242699	1.844353
	2.796853	1.403075	7.889070	7.110498	27.357372	0.513815	0.405901	0.297921
	1.067984	0.615058	1.074564	0.881649	8.777516	0.181426	0.152493	0.118320
	0.089296	0.079819	0.100570	0.071931	2.207277			
p					0.856332			
					0.285539			
	15.697773	12.735518	9.027695	8.522718	32.550596	3.072101	1.990604	2.352428
	4.845832	7.841324	7.017059	6.367880	8.243640	0.884974	0.730201	2.112542
	2.051231	2.059426	1.700217	1.563265	2.680246	0.332008	0.273074	0.317604
d	0.786717	0.972083	0.816323	0.752719	0.946767	0.113019	0.095219	0.103370
	0.231942	0.414650	0.355912	0.333105	0.339362			
					0.123510			
	31.165337	7.667041	7.744627	4.064629				
	9.334665	2.875908	3.554417	3.024025				
	3.185229	1.216434	1.168256	1.111117				
	1.021174	0.469234	0.456114	0.435905				
	0.273397	0.157971	0.153997	0.151225				

^a Valence basis set were used in conjunction with the scalar relativistic pseudopotentials of the Stuttgart group; see ref 17. ^b All electron basis set.

chainlike structures.¹⁰ In this case relativity increases the covalency of the Au–X interaction and therefore disfavors ionic structure types.

It has been suggested that relativity and dispersive type interactions (correlation effects) are responsible for aurophilic interactions.¹¹ The special role of gold in such interactions has been criticized very recently, however,¹² and it may well be the preference for gold to form two-coordinated linear structures to be the main reason for these interactions.¹³ Relativistic effects are known to be important for all group 11 elements and their compounds, especially for gold where a “relativistic maximum” is found.¹⁴ Significant changes in their chemical properties and their behavior can be observed and in the past several authors have pointed out the importance of relativity in the chemistry and physics of gold.¹⁵

Unlike molecular structures, it is currently not possible to predict solid-state structures from basic models and principles. It is therefore important to gain insight into structure and bonding of solid-state compounds. There seems also to be scarce data for the sublimation energy of group 11 halides important for discussing the stability of the solid-state compound with respect to disproportionation into the metal and the metal halide with the metal being in a higher oxidation state (e.g., CuF₂ or AuF₃). In this work, we provide theoretical data for experimentally known as well as a number of unknown solid-state modifications by quantum theoretical methods to discuss their relative stability.

Computational Details

To investigate the quite different MX (M = Cu, Ag, Au; X = F, Cl, Br, I) structure modifications, we carried out solid-state calculations for all known low pressure, several high pressure, and some experimentally unknown but nevertheless interesting modifications of the group 11 halides. The program CRYSTAL98 was used to carry out all relativistic and non-relativistic solid state and molecular calculations for the group 11 monohalides.¹⁶ Scalar relativistic energy consistent small-core Stuttgart pseudopotentials¹⁷ within density functional theory (DFT) using the B3LYP hybrid functional are used, and for comparison Hartree–Fock (HF) theory in order to get a crude estimate of electron correlation effects (assuming that B3LYP

leads to results close to experimental values). In addition, we carried out nonrelativistic calculations for the gold monohalides compounds to estimate the influence of relativistic effects. At the B3LYP level we adjusted new (5s5p5d) uncontracted valence basis sets for the neutral group 11 metals (Cu, Ag, Au) while for the halogens (Cl, Br, I) uncontracted (4s4p) valence basis sets were developed using a numerical gradient technique by minimizing the total electronic energy for the neutral atom. For fluorine, we optimized a (7s6p) all-electron basis set at the B3LYP level of theory. The exponents for these small basis sets (SB) are listed in Table 1. We note that larger basis sets with additional diffuse s and p functions causes severe SCF convergence problems as such problems are well-known in solid-state calculations using atomic basis sets (as opposed to plane waves). On the other hand, the solid-state electronic density is usually more compressed compared to the gas phase due to next neighbor interactions, and such diffuse functions may not be too important. We note that the current implementation of CRYSTAL does not allow for f- or g-projectors in the pseudopotential and is limited to basis sets up to angular momentum $l = 2$. We believe, however, that the neglect of such effects is within the error of the density functional approximation. For the gas-phase dimers B3LYP calculations with large basis sets (LB) have been carried out using f- or g-projectors for comparison. The details are described in ref 13.

The more complicated geometries of all chain structures were optimized with the program code LoptCG developed by Zicovich–Wilson.¹⁸ CuF and AuF are unknown in the solid state, while for both compounds, the corresponding structure of the chloride was used as a starting point in the geometry optimizations. The gas-phase structures of the group 11 halides were optimized as well since the total electronic energy was needed for the calculation of the cohesive energy. The basis sets used here do not lead to very accurate dipole moments. The dipole moments of the diatomics needed for our discussion were therefore derived from coupled cluster (CCSD(T)) level of theory¹⁹ using much larger basis sets to achieve reliable data (see ref 13 for details).

Results and Discussion

The test calculations for the diatomic compounds using the small basis sets (SB) as shown in Table 1 are presented in Table

TABLE 2: Calculated Spectroscopic Parameters for the Gas Phase Group 11 Halides^a

property	method	CuF	CuCl	CuBr	CuI
r_e	B3LYP/SB	1.792	2.137	2.275	2.408
	B3LYP/LB	1.755	2.070	2.193	2.370
	CCSD(T)/LB	1.753	2.066	2.178	2.346
	CCSD(T)+SO ^b	1.74	2.05	2.17	-
	expt ^c	1.745	2.051	2.173	2.338
μ_e	B3LYP/LB	4.93	4.70	4.42	4.05
	CCSD(T)/LB	5.36	5.12	4.75	4.32
	MRCISD ^b	5.80	5.70	5.55	-
	expt ^c	5.77	-	-	-
property	method	AgF	AgCl	AgBr	AgI
r_e	B3LYP/SB	2.036	2.404	2.537	2.691
	B3LYP/LB	1.996	2.314	2.428	2.620
	CCSD(T)/LB	1.987	2.295	2.400	2.562
	CCSD(T)+SO ^b	1.99	2.30	2.41	-
	expt ^c	1.983	2.281	2.393	2.545
μ_e	B3LYP/LB	5.71	5.56	5.24	4.93
	CCSD(T)/LB	6.44	5.85	5.46	4.98
	MRCISD ^b	6.75	6.74	6.61	-
	expt ^c	6.22	5.70	-	-
property	method	AuF	AuCl	AuBr	AuI
r_e	B3LYP/SB	2.027	2.354	2.512	2.634
	NR-B3LYP/SB	2.162	2.538	2.659	2.816
	B3LYP/LB	1.959	2.254	2.375	2.571
	NR-B3LYP/LB	2.123	2.456	2.567	2.757
	CCSD(T)/LB	1.930	2.226	2.339	2.506
	CCSD(T)+SO ^b	1.93	2.23	2.34	-
	expt ^c	1.918	2.199	2.318	2.471
μ_e	B3LYP/LB	4.32	3.75	3.33	2.84
	CCSD(T)/LB	4.49	3.94	3.43	2.81
	MRCISD ^b	4.89	4.91	4.55	-
	NR-B3LYP/LB	6.34	6.41	6.14	5.94

^a Bond distances r_e in Å, dipole moments μ_e in D. ^b For comparison multireference CISD and CCSD(T) plus spin-orbit results are taken from ref 22. ^c Experimental results from refs 20 and 22. SB denotes the small basis set listed in Table 1.

2 and compared to experimental results^{20,21} and recent multireference CISD calculations from Stoll et al.²² The calculated bond distances are compared with experimental values in Figure 2. It is evident that the bond distances are overestimated by 0.05–0.2 Å. This is partly due to the limited basis set used in the DFT calculations as a comparison with the B3LYP results using larger basis sets show. However, the B3LYP functional tends to overestimate the group 11 halide bond distances in general, by as much as 0.1 Å for AuI for example. We therefore expect that the calculated solid state structures have slightly overestimated bond lengths as well, which is indeed the case as shown in Figure 2. Table 2 also shows that while the dipole moments are increasing from CuX to AgX for all halides, this trend changes when going to the gold compounds due to relativistic effects.¹⁴ Hence, for the gold halides, the ionicity in the Au–X bond is greatly reduced, which has important implications for the solid state.¹⁰

In Table 3, the structural information, i.e., lattice parameters and positional parameters, and sublimation energies $\text{MX(s)} \rightarrow \text{MX(g)}$ are listed for the cubic structures of the bulk MX compounds. Two different modifications are listed here, the zinc blende and the rock salt structures known, for example, as the low-pressure and high-pressure cubic modifications for the copper halides, respectively. By comparing the corresponding sublimation energies of the different modifications, it becomes obvious that the zinc blende modification is energetically most stable for CuCl, CuBr, and CuI, in agreement with the experimental findings. The lattice parameters and subsequently

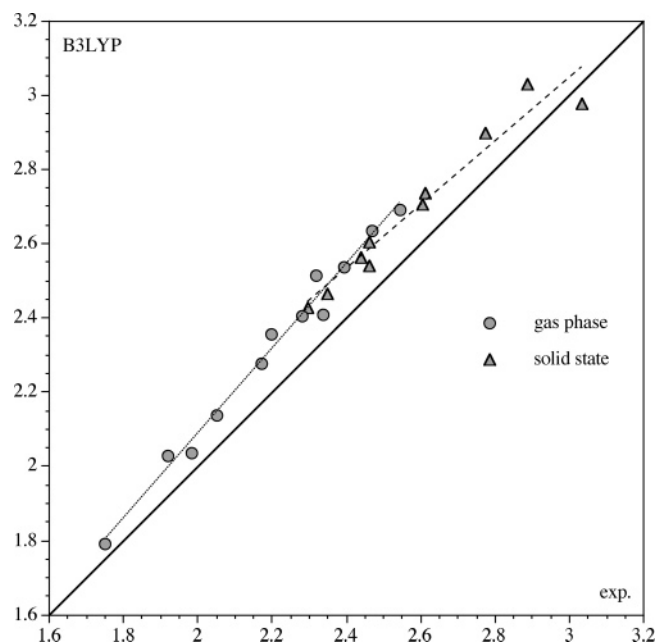


Figure 2. Calculated B3LYP bond distances using the small basis set (Table 1) against experimental values for the gas phase (diatomic) and the solid state (in Å) group 11 halides.

the Cu–X bond lengths of the zinc blende modifications turn out to be about 0.1 Å larger than the experimental values (Figure 2) for reasons as explained before. It is interesting to note that the calculated value for CuF should be around 2.33 Å (2.21 Å for the experimental values) according to a linear fit of CuCl, CuBr, and CuI, but in fact we get a Cu–F bond distance of 2.146 Å. We notice that fluorine compounds often yield bond distances different from what one expects from simple periodic trends. Anyway, if we try to make a prediction for the CuF bond distance on the basis of the experimental values, taking our mean calculation error into account, we obtain about 2.03 Å.

It is interesting to compare the results for the cubic low-pressure zinc blende and the high-pressure rock salt CuX modifications. As expected we calculate higher densities ρ and lower sublimation energies ΔE_{sub} for all rock salt modifications compared to the corresponding zinc blende structures (Table 3). We observe a clear trend going down the period from fluorine to iodine. While in the CuF case the two modifications are energetically almost degenerated (ZB 213.8 kJ mol^{−1}, RS 213.5 kJ mol^{−1}, $\Delta E = 0.3$ kJ mol^{−1}) with similar densities, the rock salt modification becomes more and more disfavored with increasing size of the halogen atom (CuCl, $\Delta E = 20.4$ kJ mol^{−1}; CuBr, $\Delta E = 25.6$ kJ mol^{−1}) and the difference amounts to 44.3 kJ mol^{−1} in the CuI case. This implies that it should become more and more difficult to achieve a phase transition from the zinc blende to the rock salt structure. Experimentally, there is at least weak evidence for this hypothesis, as Hull et al.² could measure such a phase transition for CuCl and CuBr at around 10 GPa, while no CuI rock salt modification was observed which is expected to require much higher pressures.

In contrast to copper, the silver halides crystallize at ambient conditions in a rock salt modification, with the exception of AgI where three different modifications are found. This is perfectly reproduced by our calculations (compare to the results shown in Table 4) as the rock salt modifications are always calculated to be the most stable except for AgI. In the AgI case the zinc blende (162.7 kJ mol^{−1}) and the wurzite (160.6 kJ mol^{−1}) structures are clearly more stable than the rock salt

TABLE 3: Calculated B3LYP/SB Solid State Properties the Group 11 Monohalides in (M = Cu, Ag, Au; X = F, Cl, Br, I)^a

		CuF		CuCl		CuBr		CuI	
		ZB	RS	ZB	RS	ZB	RS	ZB	RS
r	calcd	2.147	2.307	2.463	2.666	2.603	2.821	2.734	3.000
	expt			2.347	2.465 ^b	2.461	2.585 ^b	2.612	
a	calcd	4.957	4.614	5.688	5.331	6.010	5.642	6.313	5.999
	expt			5.420	4.929 ^b	5.684	5.170 ^b	6.032	
ΔE_{sub}	calcd	213.8	213.5	187.7	161.3	176.5	150.9	165.4	121.1
ρ	calcd	5.54	5.58	3.57	4.34	4.39	5.31	5.03	5.86
	expt			4.13	5.49	5.19	6.89	5.76	
		AgF		AgCl		AgBr		AgI	
		ZB	RS	ZB	RS	ZB	RS	ZB	RS
r	calcd	2.376	2.541	2.724	2.896	2.838	3.029	2.976	3.191
	expt		2.460		2.775		2.888		3.017 ^c
a	calcd	5.487	5.081	6.290	5.791	6.554	6.057	6.872	6.382
	expt		4.920		5.549		5.775		6.034 ^c
ΔE_{sub}	calcd	203.5	212.2	181.7	184.8	169.5	169.5	162.7	148.6
$\Delta H_{\text{sub}}(T)$	expt		179		199		198		144
ρ	calcd	5.10	6.42	3.83	4.90	4.43	5.61	4.81	6.00
	expt		7.07		5.57		6.47		7.10
		AuF		AuCl		AuBr		AuI	
		ZB	RS	ZB	RS	ZB	RS	ZB	RS
r	calcd	2.465	2.601	2.735	2.929	2.856	3.038	2.928	3.232
a	calcd	5.693	5.201	6.316	5.858	6.595	6.075	6.763	6.463
ΔE_{sub}	calcd	139.9	146.9	140.5	138.7	138.9	126.1	143.8	104.8
ρ	calcd	7.77	10.20	6.13	7.68	6.41	8.20	6.95	7.97

^a Bond distances r and lattice constants a (in Å), sublimation energies ΔE_{sub} for $\text{MX}(\text{s}) \rightarrow \text{MX}(\text{g})$ in kJ mol^{-1} , and bulk X-ray densities ρ in g cm^{-3} for the rock salt (RS) and zinc blende (ZB) structures. ^b High-pressure modification (10 GPa) from ref 2. ^c High-pressure modification (1.5 GPa) from ref 3.

TABLE 4: Calculated B3LYP/SB Properties for the Wurtzite Phase of the Group 11 Iodides^a

	CuI	AgI	AuI
r_1	2.741	2.918	3.029
r_2	2.727	2.976	2.955
a	4.451	4.918	4.930
c	7.309	7.616	7.649
ΔE_{sub}	167.1	160.6	143.3
ρ	5.04	4.89	6.68

^a Bond distances r and lattice parameters a and c in Å, sublimation energies ΔE_{sub} for $\text{MI}(\text{s}) \rightarrow \text{MI}(\text{g})$ (M = Cu, Ag, Au) in kJ mol^{-1} , and bulk densities ρ in g cm^{-3} . For this modification there are two different M–I distances with r_1 describing one bond and r_2 three bonds.

modification (148.6 kJ mol^{-1}), which is only known as a high-pressure modification. Completely analogous to the copper halides, we observe a similar trend for the AgX compounds; namely, the rock salt structures become more and more unfavorable compared to the cubic zinc blende with increasing size of the halide. For AgBr the zinc blende modification already shows a similar stability compared to the rock salt structure according to our calculations.

In contrast to the CuX (X = Cl, Br, I) case where 6-fold rock salt modifications can be observed under high pressure, for silver the coordination sphere is expanded to eight if pressure is applied. According to Hull et al. the phase transitions occur most likely from the 6-fold rock salt modification via the KOH-like (distorted rock salt structure, 6-fold coordination) and the orthorhombic TII-type structure (7-fold coordination) before an 8-fold CsCl modification can be observed.² In this context it is interesting to compare the phase transition of AgF with AgCl. It is known from experiment that for AgF pressures of at least 2.7 GPa are needed to achieve a phase transition into the CsCl structure, while for AgCl this occurs at even higher pressures, i.e., ~ 17 GPa. If we now assume that a larger transition pressure

corresponds to a larger energy difference between the rock salt NaCl and the CsCl modification, we should be able to confirm this from our calculations. For AgF, we obtain a moderate energy difference of $\Delta E = 18.4 \text{ kJ mol}^{-1}$ between both modifications (RS 212.2 kJ mol^{-1} , CsCl 193.8 kJ mol^{-1}), while for AgCl a much larger energy difference of $\Delta E = 32.7 \text{ kJ mol}^{-1}$ is obtained (RS 184.8 kJ mol^{-1} , CsCl 152.1 kJ mol^{-1}). Similar results were reported by Nunes et al.⁶ Using the local density approximation (LDA) method they also found a preference of the CsCl modifications at higher pressures.

The change in volume is another important indication for a phase transition at higher pressures. For AgF and AgCl we derive the densities from our optimized structures as shown in Table 3. For the CsCl modifications we obtain $\rho = 7.451 \text{ g cm}^{-3}$ for AgF and 5.358 g cm^{-3} for AgCl, a change from the more stable rock salt structures of $\Delta\rho = 1.028 \text{ g cm}^{-3}$ for AgF and 0.457 g cm^{-3} for AgCl. This gives a volume change of $\Delta V = -2.6 \text{ cm}^3 \text{ mol}^{-1}$ for AgF and $-2.5 \text{ cm}^3 \text{ mol}^{-1}$ for AgCl. For AgCl this leads to $\Delta V/V_0 = -0.085$ in reasonable agreement with the LDA result of Nunes and Allen (-0.071).⁶ By using the well-known thermodynamic expression, $P = -dU/dV \approx \Delta(\Delta E_{\text{sub}})/\Delta V$, we obtain a phase transition pressure of 7 GPa for AgF and 13 GPa for AgCl from our B3LYP results, in qualitative agreement with experimental values.

For gold, the chainlike I or P structures (Figure 1) are clearly favored compared to the cubic structures.^{23–27} These chainlike structures are often reported as rather unusual compared to typical binary ionic compounds. The energy differences between chainlike and next stable either rock salt or zinc blende modification are indeed quite large for AuF, $\Delta(\Delta E_{\text{sub}}) = 35.2 \text{ kJ mol}^{-1}$, which is unknown in the solid state, but much smaller for the heavier gold halides, i.e., 18.9 (AuCl), 15.0 (AuBr), and only 4.1 kJ mol^{-1} (AuI). Interestingly, some of the cubic higher energy structures also have lower densities, i.e., compare the

TABLE 5: Scalar-Relativistic and Nonrelativistic Hartree–Fock (HF) and DFT (B3LYP) Results for the Chainlike AuX Compounds at the B3LYP/SB Level of Theory^a

	AuF		AuCl		AuBr		AuI	
	B3LYP		HF	B3LYP	HF	B3LYP	HF	B3LYP
Relativistic								
<i>a</i>	6.301	7.795	6.740	5.006	4.305	5.000	4.351	
<i>c</i>	8.000	9.224	8.699	12.400	12.149	14.000	13.730	
<i>c/z</i>	0.180	0.159	0.201	0.152	0.170	0.146	0.162	
<i>r</i> (AuX)	2.136	2.439	2.427	2.584	2.563	2.703	2.707	
<i>r</i> (AuX) _{expt}			2.296		2.438		2.603	
<i>r</i> (AuAu)	2.994	3.593	3.226	3.540	3.044	3.536	3.076	
	3.151	3.897	3.370					
ΔE_{sub}	182.1	136.5	159.4	128.2	153.9	119.7	147.9	
ρ	9.03	5.51	7.81	5.92	8.17	6.15	8.28	
Nonrelativistic								
<i>a</i> [Å]	6.309	7.502	6.741	5.001	4.337	5.000	4.353	
<i>c</i> [Å]	8.004	9.501	8.700	12.400	12.152	14.000	13.730	
<i>c/z</i>	0.197	0.191	0.215	0.170	0.152	0.162	0.171	
<i>r</i> (AuX)	2.240	2.610	2.517	2.751	2.672	2.878	2.811	
<i>r</i> (AuAu)	2.997	3.560	3.227	3.536	3.067	3.536	3.077	
	3.155	3.751	3.371					
ΔE_{sub}	122.6	87.4	102.9	87.5	100.4	76.2	90.2	
ρ	9.01	5.77	7.81	5.93	8.05	6.15	8.27	

^a Calculated bond distances *r* and lattice parameters *a* and *c* in Å, sublimation energies ΔE_{sub} for AuX(s) → AuX(g) in kJ mol^{−1}, and bulk densities ρ in g cm^{−3}. For AuF and AuCl the chain-I structure and for AuBr and AuI the chain-P structure were taken (see Figure 1). For AuBr, we have $\rho = 8.19$ g cm^{−3} for the chain-I structure.

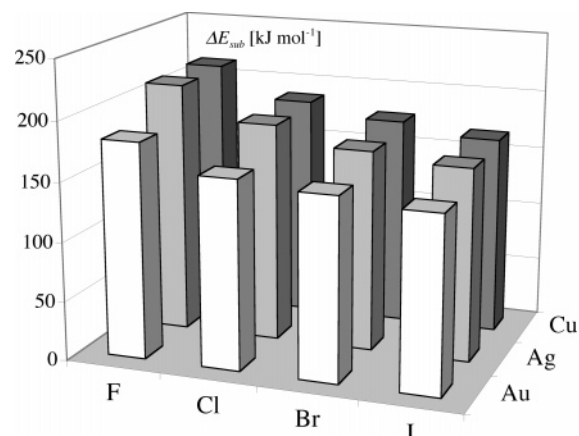
values in Tables 3 and 5. For example, for AuI where the energy difference between the different modifications is quite small, both the ZB and RS structures have lower densities. This implies that a phase transition into the cubic structure through higher pressures may not be possible. For AuBr both the chain-I and chain-P structures are observed with very similar densities, but quite different Au–Br–Au angles and Au–Au bond distances. For the chain-P structure of AuBr, we have *r*(Au–Au) = 3.04 Å from experiment in excellent agreement with our calculated B3LYP value. For AuI the experimental Au–Au distance is 3.08 Å, again in perfect agreement with our value. This is somehow surprising since aurophilic interactions are not so well described within the various density functional approximations currently in use.

If we also consider chainlike modifications for the lighter group 11 compounds, we obtain sublimation energies for the copper halides which are energetically between the zinc blende and rock salt structures (see ref 10 for more details). From a simple energetic point of view this means that under pressure a transition from a zinc blende to a chainlike arrangement may occur, and in fact there is some evidence for intermediate phases on the transformation to the rock salt modification. However, we cannot confirm at this point that such arrangements represent local minima under high pressures. Nevertheless, considering the known experimental findings, the lower coordination sphere and the calculated lower densities rule out such a chainlike arrangement for the lighter group 11 halides. In particular for the silver halides, the chainlike arrangements are up to 50–60 kJ mol^{−1} higher in energy compared to the cubic arrangements, and it is therefore highly unlikely that such modifications can be observed experimentally. Different from the AuX compounds, the CuX and AgX halides can be regarded as mainly ionic. This is evident from a Mulliken population analysis where we see a sharp drop in the metal charge going down the group 11 series of halides, i.e., *q*(Cu) = 0.58 for CuF (RS), *q*(Ag) = 0.77 for AgF (RS), and *q*(Au) = 0.40 for AuF (chain-I). Similar trends are observed for the other halides.

TABLE 6: Scalar-Relativistic and Nonrelativistic Hartree–Fock (HF) Results for the Hypothetical Rock Salt AuX Compounds^a

	AuF		AuCl		AuBr		AuI	
	NR	R	NR	R	NR	R	NR	R
<i>a</i>	5.407	5.271	6.212	6.008	6.500	6.237	6.873	6.709
<i>r</i>	2.704	2.636	3.106	3.004	3.250	3.118	3.436	3.355
ΔE_{sub}	226.6	169.6	200.2	142.9	185.2	125.3	169.8	108.1
ρ	9.07	9.80	6.44	7.14	6.70	7.58	6.63	7.12

^a Calculated bond distances *r* and lattice parameters *a* in Å, sublimation energies ΔE_{sub} for AuX(s) → AuX(g) in kJ mol^{−1}, and bulk densities ρ in g cm^{−3}. For the B3LYP results, see Table 3.

**Figure 3.** Calculated sublimation energies ΔE_{sub} (in kJ mol^{−1}) for the most stable modifications of all group 11 halides.

A comparison between the relativistic and nonrelativistic B3LYP values clearly points toward relativistic effects being responsible for the change to the unusual chainlike structure as pointed out before. Relativistic destabilization of the cubic and relativistic stabilization of the chainlike structures due to a decrease (increase) in ionicity (covalency) in the AuX interactions are the main reason for this structural difference.¹⁰ In Table 6, we include the HF results for the hypothetical rock salt structures of all gold halides which can be compared to the HF results for the chainlike structures in Table 5. For AuCl it is the rock salt structure which is more stable at the HF level, and one can conclude that it is electron correlation effects that are responsible for the chainlike structures. This has been pointed out previously by Doll et al.⁹ Hence, the interpretation depends on which perturbation is considered first one has two alternative but equally valid interpretations. At the nonrelativistic HF level the rock salt structure is now clearly favored for all gold halides, and it is well-known that electron correlation and relativistic effects are not additive. However, at the relativistic HF level the difference between the chainlike and rock salt structures are not that big, and for AuBr and AuI, it is already the chainlike structure which becomes more stable. We mention that for AuF the AuCl structure type is not stable any more at the HF level and is therefore not included in Table 5. The calculation resulted in the formation of linear F–Au–F–Au chains instead of the zigzag chains.

Finally we discuss the trend in sublimation energies, MX(s) → MX(g) + ΔE_{sub} , for the most stable modifications of the gold halides, Figure 3. We mention that these are 0 K values and do not include finite temperature corrections, as this would not be easy to obtain for the solid state and the errors introduced by the limited basis sets used are by far greater. However, they can be used for the calculation of lattice energies since the dissociation energies of the diatomic group 11 halides in the

gas phase are rather well-known.^{17,20} There is a clear and smooth trend down the group 11 elements for ΔE_{sub} , i.e., $\text{Cu} > \text{Ag} > \text{Au}$, and down the group 17 elements, i.e., $\text{F} > \text{Cl} > \text{Br} > \text{I}$, with the highest sublimation energy calculated for CuF (213.8 kJ mol^{-1}) and the lowest for AuI (147.9 kJ mol^{-1}). This may be quite surprising considering that relativistic effects are so important for gold compounds and often anomalies in periodic trends are seen.²⁸ Relativistic effects lower the sublimation energies due to reduced ionic interactions (the nonrelativistic B3LYP results for the rock salt modification are $\Delta E_{\text{sub}} = 227.3 \text{ kJ mol}^{-1}$ for AuF , 204.6 kJ mol^{-1} for AuCl , 187.7 kJ mol^{-1} for AuBr , and 173.0 kJ mol^{-1} for AuI).

Experimental values for ΔH_{sub} are scarce and these values are influenced by the formation of dimers, trimers or even tetramers of MX in the gas phase.¹³ For the silver halides we included ΔH_{sub} values in Table 3 which are in reasonable agreement with our values despite the small basis sets applied in this study. For example, for AgF no cluster formation in the gas phase was observed at higher temperatures by mass spectrometric studies²⁹ and a $\Delta H_{\text{sub}}(T)$ value of $200 \pm 20 \text{ kJ mol}^{-1}$, which compares to our B3LYP value of 212 kJ mol^{-1} .

Conclusion

From the calculated sublimation energies for a number of different modifications we were able to reproduce the correct order of stability for the experimentally known crystal structures. It is however difficult (if not impossible) to predict from simple bonding arguments which the most stable modification is. In the case of the copper or silver halides the solid-state structures follow more the ionic model with the silver halides preferring the simple rock salt modification. In contrast the unusual chainlike structures for the gold halides comes from a change to more covalent Au-X interactions with short Au-Au distances, which is probably best described by the influence of relativity. It would be useful to determine more accurate sublimation energies from experiment in order to discuss the reliability of the density functional approach chosen in our investigation and to improve on the basis sets and pseudopotentials used. It would also be interesting to investigate the gold halides at higher pressures in order to see if significant phase transitions take place.

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References and Notes

- (1) von Wartenberg, H. Z. *Anorg. Allg. Chem.* **1939**, 241, 381.
- (2) Hull, S.; Keen, D. A. *Phys. Rev. B* **1994**, 50, 5868.
- (3) Hull, S.; Keen, D. A. *Phys. Rev. B* **1999**, 59, 750.
- (4) Halleck, P. M.; Jamieson, J. C.; Pistorius, C. W. F. T. *J. Phys. Chem. Solids* **1972**, 33, 769.
- (5) Bridgman, P. W. *Proc. Am. Acad. Sci.* **1945**, 76, 1.
- (6) Nunes, G. S.; Allen, P. B.; Martins, J. L. *Phys. Rev. B* **1998**, 57, 5098.
- (7) Hull, S.; Berastegui, P. *J. Phys.: Condens. Matter* **1998**, 10, 7945.
- (8) Lawaetz, P. *Phys. Rev. B* **1972**, 5, 4039.
- (9) Doll, K.; Pykkö, P.; Stoll, H. *J. Chem. Phys.* **1998**, 109, 2339.
- (10) Söhlne, T.; Hermann, H.; Schwerdtfeger, P. *Angew. Chem., Int. Ed.* **2001**, 40, 4381.
- (11) (a) Pykkö, P.; Mendizabal, F.; Fernando, M. *Chem.—Eur. J.* **1997**, 3, 1451. (b) Pykkö, P.; Zhao, Y. *Angew. Chem., Int. Ed. Engl.* **1991**, 30, 604.
- (12) O'Grady, E.; Kaltsonyannis, N. *Phys. Chem. Chem. Phys.* **2004**, 6, 680.
- (13) Schwerdtfeger, P.; Krawczyk, R. P.; Hammerl, A.; Brown, R. *Inorg. Chem.* **2004**, 43, 6707.
- (14) (a) Pykkö, P. *Chem. Rev.* **1988**, 88, 563. (b) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, 91, 1762.
- (15) Pykkö, P. *Angew. Chem., Int. Ed.* **2004**, 43, 4412.
- (16) Saunders, V. R.; Dovesi, R.; Roetti, C.; Causà, M.; Harrison, N. H.; Orlando, R.; Zicovich-Wilson, C. M. *Program CRYSTAL98*, University of Torino, Torino, Italy, 1998.
- (17) (a) Bergner, A.; Dolg, M.; Küchle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, 80, 1431. (b) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, 86, 866. (c) Andrae, D.; Haeussermann, U.; Dolg, M.; Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, 75, 173. (d) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, 91, 1762.
- (18) Zicovich-Wilson, C. M. *Program LoptCG*, Instituto de Tecnologia Química U.P.V.-C.S.I.C.: Valencia, Spain, 1998.
- (19) Gaussian 98, Revision A.9. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1998.
- (20) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, Constants of Diatomic Molecules*, Van Nostrand: New York, 1979.
- (21) Evans, C. J.; Gerry, M. C. L. *J. Chem. Phys.* **2000**, 112, 9363.
- (22) Guichemerre, M.; Chambaud, G.; Stoll, H. *Chem. Phys.* **2002**, 280, 71.
- (23) Janssen, E. M. W.; Folmer, J. C. W.; Wiegers, G. A. *J. Less Common Met.* **1974**, 38, 71.
- (24) Strähle, J.; Lörchner, K. P. Z. *Naturforsch. B* **1974**, 29, 266.
- (25) Weiss, A.; Weiss, A. Z. *Naturforsch. B* **1956**, 29, 604.
- (26) Jagodzinski, H. Z. *Kristallogr. Kristallogom. Kristallophys. Kristallochem.* **1959**, 112, 80.
- (27) Janssen, E. M. W.; Wiegers, G. A. *J. Less Com. Met.* **1978**, 57, P47.
- (28) Schwerdtfeger, P. *Heteroatom Chem.* **2002**, 13, 578.
- (29) Zmbov, K. F.; Margrave, J. L. *J. Phys. Chem.* **1967**, 71, 446.