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Pressure-Induced Changes in the Structure and Band Gap of $CsGeX_3$ (X = Cl, Br) Studied by Electronic Band Structure Calculations

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Tight-binding electronic band structures of cesium trihalometalates $CsGeX_3$ (X = Cl, Br) were calculated to examine the pressure-dependence of their crystal structures and band gaps as well as their primitive cubic to rhombohedral structural phase transitions. In agreement with experiment, our calculations show that an increase in the applied pressure decreases the band gap and the stability of $CsGeX_3$, and the band gap is larger for $CsGeCl_3$ than for $CsGeBr_3$. $CsGeCl_3$ has a much stronger second-order Jahn−Teller instability than does $CsGeBr_3$ and therefore can adopt a disordered cubic phase unlike $CsGeBr_3$.

1. Introduction

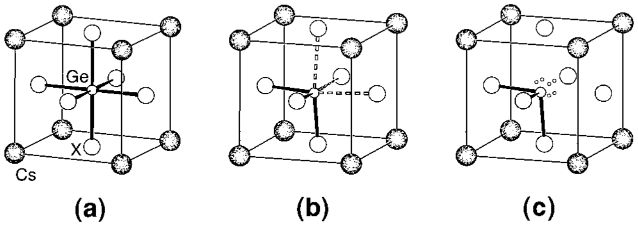
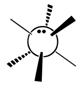


Figure 1. Schematic views of the coordinate environments of the GeX_6 octahedra in the (a) primitive cubic, (b) rhombohedral, and (c) disordered cubic phases of $CsGeX_3$. In c the small circles represent seven other positions equally available for Ge.

Cesium trihalometalates $CsMX_3$ of group 14 elements (M = Ge, Sn, Pb; X = Cl, Br, I) have M^{2+} (ns^2) cations and crystallize in perovskite variants. Under ambient conditions $CsMX_3$ adopts a rhombohedral structure. A phase transition from the rhombohedral to primitive cubic structure can be induced by applying pressure and/or raising temperature. Structural phase transitions of $CsMX_3$ lead to interesting changes in their physical properties, so $CsGeX_3$,[3−8] $CsSnX_3$,[9−20] and $CsPbX_3$ [12,21−25] have been the subject of numerous experimental studies. The crystal structure of a primitive cubic perovskite $CsMX_3$ is obtained by sharing the corners of MX_6 octahedra (Figure 1a). The major character of the HOMO of a regular MX_6^{4-} octahedron is the valence *n*s orbital of M^{2+} (i.e., an inert pair, **1a**), and that of its LUMO is the valence np orbitals of M^{2+}. Owing to a second-order Jahn−Teller (SOJT) instability,[1] the MX_6^{4-} units of $CsMX_3$ under ambient conditions adopt a distorted octahedral structure in which the M^{2+} ion is displaced toward the center of one of the eight faces of the octahedron (Figure 1b),[3,4] so that the HOMO of a distorted MX_6^{4-} becomes s/p hybridized (i.e., a lone pair, **1b**), and three short and three long M−X bonds occur at each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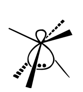
1b

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MX_6 octahedron. When the M^{2+} ion displacements are ordered to have a ferroelectric arrangement, $CsMX_3$ adopts a rhombohedral structure.[3,4] Recently, Schwarz et al. examined how the crystal structures and optical-absorption gaps of $CsGeCl_3$ and $CsGeBr_3$ depend on applied pressure.[3,4] Their studies revealed that the band gaps of $CsGeCl_3$ and $CsGeBr_3$ decrease gradually with increasing applied pressure, but $CsGeCl_3$ and $CsGeBr_3$ do not become metallic for pressures up to 30 GPa. As the applied pressure increases, $CsGeBr_3$ undergoes a phase transition from the rhombohedral (Figure 1b) to primitive cubic structure (Figure 1a) at ~1 GPa at room temperature.[3,4] $CsGeCl_3$ also undergoes a pressure-induced phase transition to a primitive cubic phase near 3 GPa at room temperature. Unlike the case of $CsGeBr_3$, however, $CsGeCl_3$ has an intermediate phase between ~0.7 and ~3 GPa, i.e., a disordered cubic phase (Figure 1c), in which each Ge occupies randomly one of the eight equivalent off-centered positions.[3]

Electronic band structure studies were carried out for $CsGeBr_3$[3] and $CsSnBr_3$.[26−28] The primitive cubic structure of $CsSnBr_3$ was predicted to be metallic in the extended Hückel calculations of Perry et al.[26] and the pseudopotential calculations of Lefevre et al.,[27] while it is predicted to be semiconducting in the linear-muffin-tin-orbital calculations of Bose et al.[28] The latter is consistent with the electrical conductivity measurements by Clark et al.[29] The band calculations of Schwarz et al.[3] using the Hartree−Fock method show that the primitive cubic structure of $CsGeBr_3$ has a band gap, but this method predicts a band gap even for a metallic compound. So far, the pressure-dependence of the band gap, the stability of the primitive cubic and rhombohedral phases, and the cause for the disordered cubic phase in $CsGeCl_3$ have not been examined in terms of electronic band structure calculations. In the present work, we probe these questions by performing extended Hückel tight binding (EHTB) calculations[30] for rhombohedral and primitive cubic structures of $CsGeX_3$ (X = Cl, Br) and by analyzing the orbital character of the levels responsible for their band gaps.

2. Electronic Band Structures

In the present EHTB calculations, double-ζ Slater-type orbitals were used for Ge, and single-ζ Slater-type orbitals were used for Cl and Br.[31] The atomic parameters employed in our study are listed in Table 1.[32] As representative examples of the electronic structures calculated for $CsGeX_3$ (X = Cl, Br), Figures 2a and 2b respectively show the dispersion relations of the electronic bands calculated for the rhombohedral (at ambient pressure) and primitive cubic (at 1.2 GPa) structures of $CsGeBr_3$.[3,4] As already found for $CsGeBr_3$[3] and $CsSnBr_3$,[27] a direct band gap occurs at R. Tables 2a and 2b summarize the relative energies and band gaps calculated for the rhombohedral and primitive cubic structures of $CsGeX_3$ (X = Cl, Br). Our calculations reveal that an increase in the applied pressure decreases the band gap and the stability of $CsGeX_3$ and that the band gap is slightly larger for $CsGeCl_3$ than for $CsGeBr_3$. These results are in good agreement with experiment.[3,4]

Table 1. Exponents ζ_i and Valence Shell Ionization Potentials H_{ii} of Slater-Type Orbitals χ_i Used for Extended Hückel Tight-Binding Calculations[a]

atom	χ_i	H_{ii} (eV)	ζ_i	c_1[b]	ζ_i'	c_2[b]
Ge	4s	−16.0	2.699	0.5485	1.575	0.5283
Ge	4p	−9.00	2.289	0.4592	1.252	0.6331
Cl	3s	−26.3	2.183	1.0		
Cl	3p	−14.2	1.733	1.0		
Br	4s	−22.7	2.588	1.0		
Br	4p	−13.1	2.131	1.0		

[a] H_{ii}'s are the diagonal matrix elements $\langle\chi_i|H^{eff}|\chi_i\rangle$, where H^{eff} is the effective Hamiltonian. [b] Contraction coefficients used in the double-ζ Slater-type orbital.

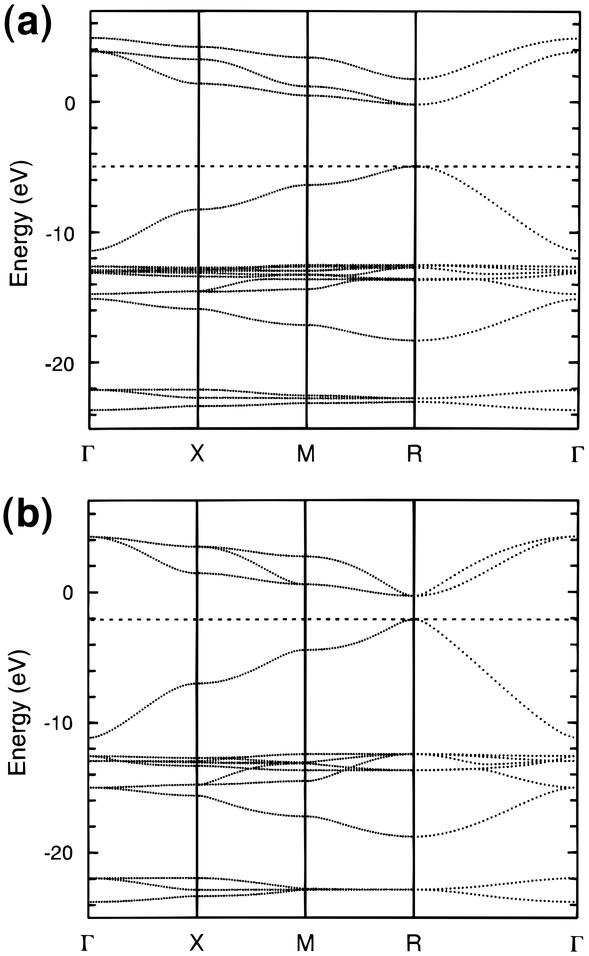
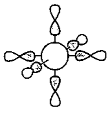


Figure 2. Dispersion relations of the electronic band structures calculated for the (a) ambient pressure and (b) 1.2 GPa structures of $CsGeBr_3$, where the dashed line refers to the highest occupied level. For the purpose of clarity, only the energy bands in the vicinity of the band gap are presented: $\Gamma = (0, 0, 0)$; $X = (a^*/2, 0, 0)$; $M = (a^*/2, b^*/2, 0)$; and $R = (a^*/2, b^*/2, c^*/2)$.

3. Orbital Character of the Levels Forming the Band Gap and Its Consequences

To understand the dependence of the band gap on applied pressure, we examine the orbitals of the band levels that determine the gap for a primitive cubic structure of $CsGeX_3$ (Figure 2b). The top of the valence band is described by the orbital **2**, in which each Ge 4s orbital makes σ antibonding



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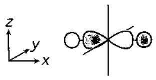
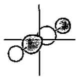
interactions with the p orbital of every X atom surrounding the Ge (hereafter referred to as the s* level). The bottom of the conduction band is triply degenerate. The three degenerate orbitals (**3a**−**c**) are obtained when each Ge 4p orbital makes σ



3a



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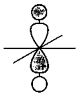

3c

antibonding interactions with the s orbitals of the two adjacent X atoms lying along the principal direction of the Ge 4p orbital (hereafter referred to as the p* levels). Thus, each Ge atom has antibonding interactions with six adjacent X atoms in the s* level, and with two adjacent X atoms in each p* level. A band gap results when the s* level lies lower than the p* level, which occurs if the energy difference between Ge 4s and Ge 4p levels is large enough. When the latter condition is not met, the p* level lies lower than the s* level. This predicts a metallic character for $CsGeX_3$ because there are only two electrons to fill the triply degenerate p* level. A similar reasoning is also applicable to $CsSnBr_3$, when the Sn 5s and Sn 5p orbitals are used in constructing the s* and p* levels, respectively. In the calculations of Perry et al.[26] and Lefevre et al.,[27] metallic character was predicted for $CsSnBr_3$ because the p* level lies lower than the s* level. The electrical conductivity measurements by Clark et al.[29] suggest that $CsSnBr_3$ is a semiconductor, which is reproduced by the calculations of Bose et al.[28]

An increase in the applied pressure decreases the cell parameter of primitive cubic $CsGeX_3$ and hence the Ge−X bond length.[3,4] The s* and p* levels have antibonding interactions between Ge and X, so they are both raised in energy by an increase in the applied pressure (Figures 3a and 3b). This energy raising is slightly larger for the s* level than for the p* level, since each Ge has more antibonding interactions with the surrounding X atoms in the s* level. Thus the band gap of the primitive cubic structure decreases somewhat as the external pressure increases, which is in agreement with experiment.

The energy difference between the valence *n*s and *n*p levels of Ge, Sn, and Pb are quite large (e.g., about 7 and 6 eV for Ge and Sn, respectively[31]). Therefore, it is expected that the s* level lies lower than the p* level in $CsMX_3$, and this relative ordering remains the same even when the cell parameter is reduced under applied pressure. Consequently, it is doubtful that $CsMX_3$ can become metallic under applied pressure. Nevertheless, $CsMX_3$ compounds can become a semiconductor with small band gap. In general, compounds with small band gap can exhibit a poor metallic behavior if they contain impurities. This may be the case for $CsGeI_3$, which was reported to be metallic.[6]

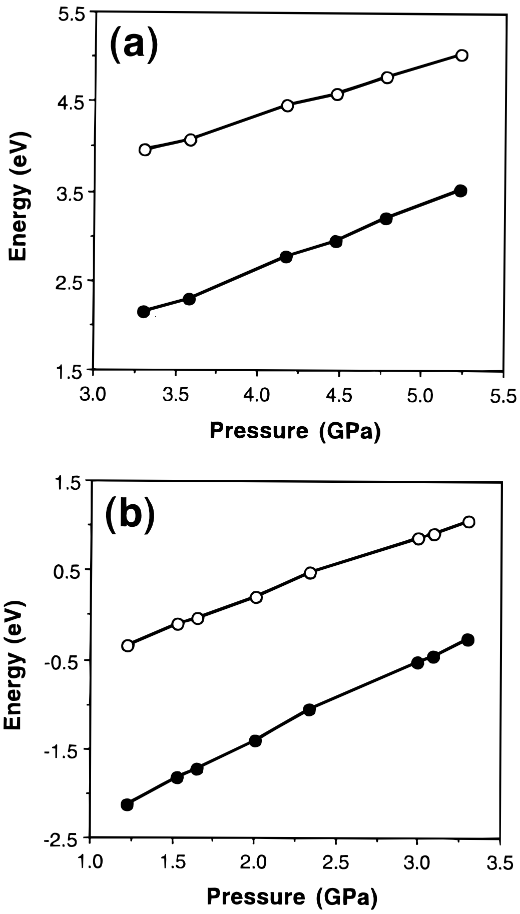

Figure 3. Top of the s* band (filled circle) and bottom of the p* band (empty circle) calculated for the primitive cubic structures of (a) $CsGeCl_3$ and (b) $CsGeBr_3$ as a function of the applied pressure.

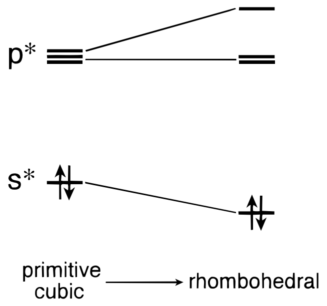

Figure 4. Schematic diagram showing how the s* and p* levels of the primitive cubic structure are related to those of the rhombohedral structure in $CsGeX_3$.

4. Causes for Structural Phase Transitions

When the structure of $CsGeX_3$ changes from primitive cubic to rhombohedral, the s* level is lowered in energy while the degenerate p* level is split into a two-below-one pattern (Figure 4). This structural transition is an SOJT distortion, and it increases the band gap. Our calculations show that under 3.3 GPa the primitive cubic structure is less stable than the rhombohedral structure by 7.0 eV per formula unit for $CsGeCl_3$ but by 5.1 eV per formula unit for $CsGeBr_3$ (Table 2). This is consistent with the observations that the rhombohedral to primitive cubic structural transition occurs at a lower applied pressure for $CsGeBr_3$ and that the extent of a local SOJT distortion, as measured by the ratio of the long to short Ge−X bonds, is greater for X = Cl than for X = Br (1.317 versus 1.230).[2b] These results show that $CsGeCl_3$ has a greater SOJT instability than does $CsGeBr_3$. Furthermore, from the viewpoint of close packing the Cs^+, M^{2+}, and X^- ions, the primitive cubic structure becomes more favorable as the tolerance factor τ,

$$\tau = \frac{r_{Cs} + r_M}{\sqrt{2}(r_M + r_X)},$$

approaches 1 where r_{Cs}, r_M, and r_X are ionic radii of the Cs^+, M^{2+}, and X^- ions, respectively. From the ionic radii of these ions (1.88, 0.73, 1.81, and 1.96 Å for Cs^+, Ge^{2+}, Cl^-, and Br^-, respectively),[33] the τ value is calculated to be larger than 1 for

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Table 2. Relative Energies, Band Gaps, and Cell Parameters of Several Structures of $CsGeCl_3$ and $CsGeBr_3$

pressure	cell parameters	relative energy (eV/FU)[a]	band gap (eV) calcd	band gap (eV) exptl
		(a) $CsGeCl_3$		
ambient	$a = 5.434$ Å	0.0	7.91	3.67
3.3 GPa	$a = 5.18$ Å	7.0	1.81	1.93
5.2 GPa	$a = 5.11$ Å	9.3	1.49	1.34
		(b) $CsGeBr_3$		
ambient	$a = 5.635$ Å	0.0	4.74	2.32
1.2 GPa	$a = 5.47$ Å	2.8	1.78	1.59
3.3 GPa	$a = 5.35$ Å	5.1	1.31	0.89

[a] FU refers to formula unit, and the energy is reported with respect to that of the structure at ambient pressure.

both $CsGeBr_3$ and $CsGeCl_3$ (1.009 and 1.027, respectively). Thus if the Ge^{2+} ion is placed at the center of an octahedron made up of six X^- ions, the resulting Ge−X distance is longer than the optimal distance so that the Ge^{2+} ion tends to stay away from the central position. Since $CsGeCl_3$ has a larger τ value than does $CsGeBr_3$, the tendency to adopt a primitive cubic structure is weaker for $CsGeCl_3$. This enhances an SOJT instability of $CsGeCl_3$ with respect to that of $CsGeBr_3$.

As the applied pressure increases, the rhombohedral to primitive cubic phase transition takes place via a disordered cubic phase in $CsGeCl_3$, while such an intermediate phase is absent in $CsGeBr_3$. This difference can be accounted for as follows: Of the Cs^+, Ge^{2+}, and X^- ions making up $CsGeX_3$, the Ge^{2+} ion is the smallest. The primitive cubic structure of $CsGeX_3$ results when the Cs^+ and X^- ions adopt a cubic close packed (CCP) lattice, and the smallest ions Ge^{2+} occupy the centers of the octahedral holes of this lattice. An applied pressure reduces the cell parameter, stabilizes the CCP lattice, and reduces the size of an octahedral hole. Thus under high applied pressure (above ∼3 GPa), the octahedral holes of $CsGeCl_3$ are not large enough to accommodate lone pairs, so the Ge^{2+} cations occupy the centers of the octahedral holes thereby leading to a primitive cubic structure. A decrease in pressure (between ∼0.7 and ∼3 GPa) increases the size of an octahedral hole so that a local SOJT distortion takes place while keeping the CCP lattice formed by the Cs^+ and Cl^- ions. Since the SOJT instability is strong in $CsGeCl_3$, local SOJT distortions take place without long-range order, thereby leading to a disordered cubic phase of $CsGeCl_3$. As the pressure is reduced below ∼0.7 GPa, the perovskite lattice expands further and allows a ferroelectric ordering of the local SOJT distortions, which gives rise to a rhombohedral structure. In general, an SOJT distortion cannot occur unless the electronic energy gain resulting from the distortion is greater than the energy of strain the distortion induces. Since $CsGeBr_3$ has a weaker SOJT instability than does $CsGeCl_3$, the lack of a disordered cubic phase in $CsGeBr_3$ implies that its electronic energy gain from the SOJT distortions becomes strong enough to surmount the energy of lattice strain only when the distortions are ferroelectrically ordered.

The above reasoning provides an explanation for the temperature dependence of the structural parameters of $CsGeCl_3$ below 155 °C (i.e., the temperature of the disordered cubic to rhombohedral phase transition under ambient pressure). Table 3 summarizes the cell parameters of $CsGeCl_3$ as a function of temperature, which were determined by powder X-ray diffraction measurements. As expected, the unit cell parameters and volume decrease with decreasing temperature. However, the angle α of the rhombohedral unit cell increases gradually toward 90°, i.e., the perovskite lattice becomes less rhombohedral (i.e., closer to cubic). As far as the cell parameters are concerned, a decrease in temperature is equivalent to an increase in applied pressure. Therefore, the temperature lowering has the effect of stabilizing the CCP lattice formed by the Cs^+ and Cl^- ions, which therefore increases the angle α toward 90°.

Table 3. Temperature Dependence of the Cell Parameters of $CsGeCl_3$ Determined from X-ray Diffraction Measurements[a]

T (°C)	*a* (Å)	α (deg)	*V* (Å^3)
+170	5.47(1)	90.00	163.67
+95	5.455(3)	89.60(4)	162.33
+50	5.441(3)	89.65(4)	161.11
+25	5.434(3)	89.71(3)	160.49
−36	5.422(2)	89.77(2)	159.42
−76	5.412(2)	89.81(2)	158.56
−116	5.400(2)	89.84(2)	157.50
−138	5.391(2)	89.89(1)	156.65
−150	5.378(2)	89.91(1)	155.55

[a] The values for 170 °C were determined by HT−Simon−Guinier (film; 11 indexed reflections). All other values were determined from single-crystal measurements on a four-circle diffractometer (CAD4; Mo Kα radiation; least squares of 25 high-angle reflections).

5. Concluding Remarks

In agreement with experiment, our calculations show that an increase in the applied pressure decreases the band gap and the stability of $CsGeX_3$ and that the band gap is larger for $CsGeCl_3$ than for $CsGeBr_3$. The $CsMX_3$ compounds have a band gap and are hence predicted to be nonmetals when the s* level lies lower than the p* level. This relative ordering is expected to remain unchanged for primitive cubic structures under high applied pressure. Therefore, it is unlikely that $CsMX_3$ compounds can become metallic under high laboratory-scale applied pressure. In the calculations predicting metallic character for $CsSnBr_3$, the p* level lies lower than the s* level, which is due most likely to the use of inadequate parametrization. As an applied pressure increases, $CsGeX_3$ undergoes a rhombohedral to primitive cubic phase transition via a disordered cubic phase for X = Cl, but the latter phase is absent for X = Br. Probable causes for this difference are that $CsGeCl_3$ has a much stronger SOJT than does $CsGeBr_3$ and that a high applied pressure stabilizes the CCP lattice formed by the Cs^+ and X^- ions.

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