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Effect of pressure on the optical-absorption edges of $CsGeBr_3$ and $CsGeCl_3$

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We have investigated the effect of hydrostatic pressure on the optical-absorption edges of the ferroelectric compounds $CsGeBr_3$ and $CsGeCl_3$. The absorption edge energies of the ambient pressure modifications (trigonally distorted cubic perovskite) are E_G = 2.32(5) eV and 3.67(5) eV, respectively. We find extraordinary large redshifts of the absorption edges under pressure for the distorted modifications (e.g., -0.61 eV/GPa for the bromine compound) as well as high-pressure cubic phases. Experimental results are interpreted on the basis of Hartree-Fock band structure calculations for $CsGeBr_3$ in the cubic primitive structure. The absorption edges are attributed to the lowest direct gap transition at the R point of the Brillouin zone.

I. INTRODUCTION

Cesium trihalogenometallates(II) of group-IV elements $CsMX_3$ (M=Ge, Sn, Pb; X=Cl, Br, I) crystallize at ambient conditions in cubic perovskite structures or slightly distorted variants thereof. These materials contain divalent group-IV cations. They are semiconductors with optical gaps in the visible spectral range. Excitonic effects have been investigated earlier[1,2] for thin films of the Pb compounds, and empirical as well as first-principles band structure calculations have been reported for the Pb and Sn compounds (see, e.g., Refs. 1 and 3). As was pointed out before,[1] the general features of the electronic structure are quite similar to that of thallium halogenides crystallizing in the cubic primitive (CsCl-type) structure.

The germanium compounds can serve as model substances for investigating physical properties, since untwinned single crystals of the noncentrosymmetric low-temperature modifications can be grown from aqueous solutions.[4] At ambient conditions, $CsGeBr_3$ and $CsGeCl_3$ crystallize in space group $R3m$.[5] Figure 1 shows a unit cell of the crystal structure in the rhombohedral setting. Cesium and halogen ions form a slightly distorted cubic closest packing; germanium is enclosed by a nearly regular halogen octahedron. The Ge atoms are shifted from the center towards one face of the coordination polyhedron, resulting in the formation of a trigonal antiprism with three short and three long distances (denoted d and d').[5]

Powder x-ray diffraction studies show $CsGeBr_3$ and $CsGeCl_3$ to undergo phase transitions to high-temperature modifications with cubic metric at 510 K and 430 K, respectively.[5] However, Raman spectra of the high-temperature modifications exhibit basically the same features as the low-temperature modification.[5] Since no Raman-active modes are expected for the cubic primitive aristotype (space group $Pm\bar{3}m$), it was concluded that the cubic metric is caused by an order-disorder phase transition, where the Ge atoms occupy one of eight equivalent positions within the halogen octahedra, as indicated by the small spheres in Fig. 1. Thus the local C_{3V} symmetry of the Ge(II)-coordination polyhedra remains unchanged at the temperature-induced phase transition.

According to recent x-ray diffraction studies of $CsGeBr_3$,[6] increasing hydrostatic pressure reduces both the deviation from a cubic metric and the 3+3 splitting of the distances d(Ge-Br) and d'(Ge-Br). X-ray and Raman measurements indicate consistently a first-order phase transition at 1.0(2) GPa to a high-pressure modification with cubic metric and a primitive unit cell. Thus the crystal structure of the high-pressure polymorph is isotypic to that of the cubic primitive perovskite structure (space group $Pm\bar{3}m$). $CsGeCl_3$ also undergoes a pressure-induced phase transition to a polymorph with octahedral Ge coordination near 3 GPa (T=300 K), but in this case an intermediate cubic disordered phase (isotypic to the high-temperature phase) is observed between about 0.7 GPa and 3 GPa.[7]

In the course of the above high-pressure experiments drastic changes in color were noticed. For instance, $CsGeBr_3$ changes from yellow to black in a narrow range up to 1.5 GPa. These observations stimulated the present investigation of the optical-absorption edges of $CsGeBr_3$ and $CsGeCl_3$ under pressure. It turns out that the large absorption edge shifts to lower energy are nearly continuous across the structural phase transitions. The initial pressure coefficient of -0.6 eV/GPa for the absorption edge energy of

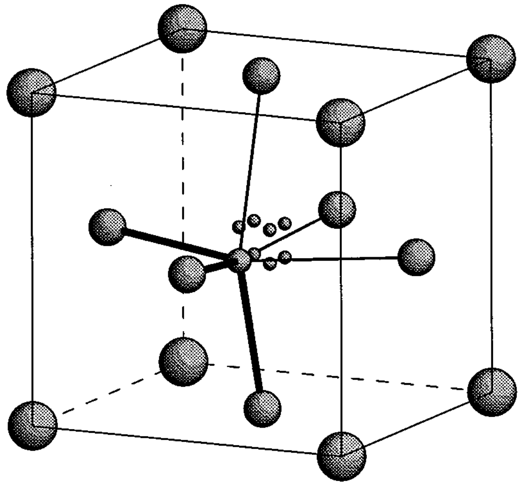

FIG. 1. Unit cell of the rhombohedrally distorted structure of $CsGeBr_3$ at ambient conditions. Small spheres indicate the eight equivalent Ge positions for the high-temperature disordered cubic phase. The displacement of the Ge atom from the center position is not drawn to scale.

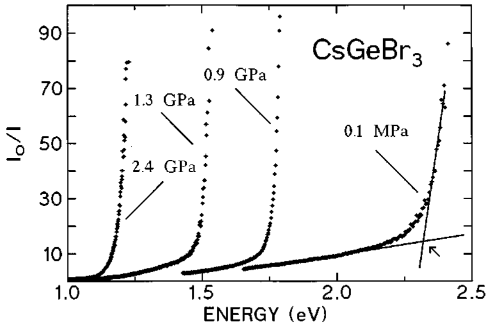

FIG. 2. Optical-absorption spectra of CsGeBr$_3$ at pressures up to 2.4 GPa. The energy of the absorption edge is taken at the point where linear extrapolations of background and steep slope intersect.

CsGeBr$_3$ is one of the largest ever observed for a band gap in a three-dimensional semiconducting material. In the case of CsGeBr$_3$, we have tested the possibility of a pressure-driven insulator-to-metal transition by performing reflectivity measurements up to 30 GPa. The experimental results for absorption edge shifts are interpreted on the basis of Hartree-Fock band structure calculations performed for CsGeBr$_3$.

II. EXPERIMENT

Crystals of CsGeBr$_3$ and CsGeCl$_3$ were synthesized from solution according to the procedures described in Ref. 5. High pressures were generated using a diamond window cell, and pressures were determined by the ruby luminescence method.[8] For absorption measurements, a small single crystal (thickness about 20 μm) was embedded in paraffin as pressure-transmitting medium. Transmission spectra were measured using a micro-optical setup which illuminates a 30 μm diameter spot on the sample. The transmitted light was dispersed by a 0.64 m grating monochromator and detected by a GaAs photomultiplier or a liquid-nitrogen-cooled Ge detector. The transmitted intensity was normalized to the intensity I_0 measured with the light beam passing through a part of the gasket hole which was not covered by the sample. Optical reflectivity was measured using a micro-optical system similar to that employed in previous high-pressure reflectivity studies.[9] A polycrystalline sample was first pre-pressed gently in order to produce a smooth surface and then mounted in the pressure cell such that the sample surface was in direct contact with one of the diamond windows. The remaining cell volume was filled with CsCl serving as a quasihydrostatic pressure medium. The absolute reflectivity at the diamond-sample interface (denoted R_d) is measured from a focal spot of about 30 μm diameter.

III. RESULTS AND DISCUSSION

Optical-absorption spectra of CsGeBr$_3$ at different pressures are shown in Fig. 2, where the inverse of the normalized transmission is plotted versus photon energy. For all pressures a well-defined absorption edge is observed. With increasing pressure the edge shows a pronounced redshift and no major change in the slope of the absorption profile. These pressure effects are reversible for decreasing pressure. The reduced transmission found in the spectra at energies below the edge is mainly attributed to grain boundary scattering. As indicated in Fig. 2, the energy of the absorption edge is taken as the point where the linear extrapolations of the flat background and the steep part of the absorption curve intersect. At ambient pressure the absorption edge energy thus obtained is 2.32(5) eV.

Figure 3(a) shows the pressure dependence of the absorption edge energies for both materials. For CsGeBr$_3$ the linear pressure coefficient in the range $P \leqslant 1$ GPa is $-0.61(2)$ eV/GPa. This is an extraordinarily large value. In fact, to our knowledge this is one of the largest band gap shifts ever observed in a three-dimensional crystalline material. Similarly large pressure coefficients have been reported for quasi-one-dimensional linear-chain compounds (see, e.g., Ref. 10). Within experimental resolution, the absorption edge energy of CsGeBr$_3$ shows no discontinuity at the structural phase transition near 1 GPa.

The ambient pressure absorption edge energy of CsGeCl$_3$ is 3.67(5) eV. The edge drops to about 3.1 eV near the rhombohedral-to-cubic disordered transition (0.7 GPa). The average linear pressure coefficient in the disordered regime (0.7 to 3 GPa) is $-0.41(4)$ eV/GPa. The experimental data indicate a small change in slope near the transition from cubic disordered to cubic primitive (3 GPa).

Figure 3(b) illustrates the dependence of the absorption edge energies on relative volume.[11] This representation suggests a method to distinguish two regimes. The low-pressure data for the rhombohedral and disordered modifications are well approximated by linear relations. Data for the cubic high-pressure phases are systematically lower in energy compared to the extrapolated low-pressure behaviors. Thus the volume dependences suggest that the first order transitions to the cubic phases involve a discontinuous lowering of the optical gaps, which is smeared out due to phase mixing. *Average* experimental gap deformation potentials $D = \Delta E_G/(\Delta V/V_0)$ (V_0 is the zero pressure volume) are 8.5(5) eV ($P \leqslant 1.0$ GPa) and 10.2(15) eV ($P \geqslant 1.5$ GPa) for CsGeBr$_3$ and 12.5(8) eV ($P \leqslant 3.0$ GPa) and 10.1(14) eV ($P \geqslant 3.5$ GPa) for CsGeCl$_3$.

The absolute values of the deformation potentials at low pressures are comparable to that of the direct gap of Ge [-9 eV (Ref. 12)] but opposite in sign. Thus the large pressure coefficients of the optical gap energies are in part a result of the large compressibility of the Cs trihalogenides.[6,7]

Given the large redshifts of the absorption edges, one might expect a band gap closure (insulator-to-metal transition) taking place at higher pressures. In the case of CsGeBr$_3$, this possibility was tested by optical-reflectivity measurements. Figure 4 shows optical-reflectivity spectra for pressures up to 20 GPa. These spectra are corrected for absorption in the diamond window and for reflection losses at its external surface. The low overall reflectivity values result from the small refractive index step at the sample-diamond interface. The qualitative observations are as follows. For pressures up to about 8 GPa, the optical transitions above the fundamental gap also shift to lower energy. However, for pressures from 8 to 12 GPa the oscillator strength below 4 eV starts to decrease rapidly. It remains to be investigated if this loss of oscillator strength in the visible and uv range is related to a phase change. Up to 30 GPa, no evidence is found for the emergence of a free carrier response in the near-infrared part of the spectrum.

Band structure calculations for CsGeBr$_3$ have been per-

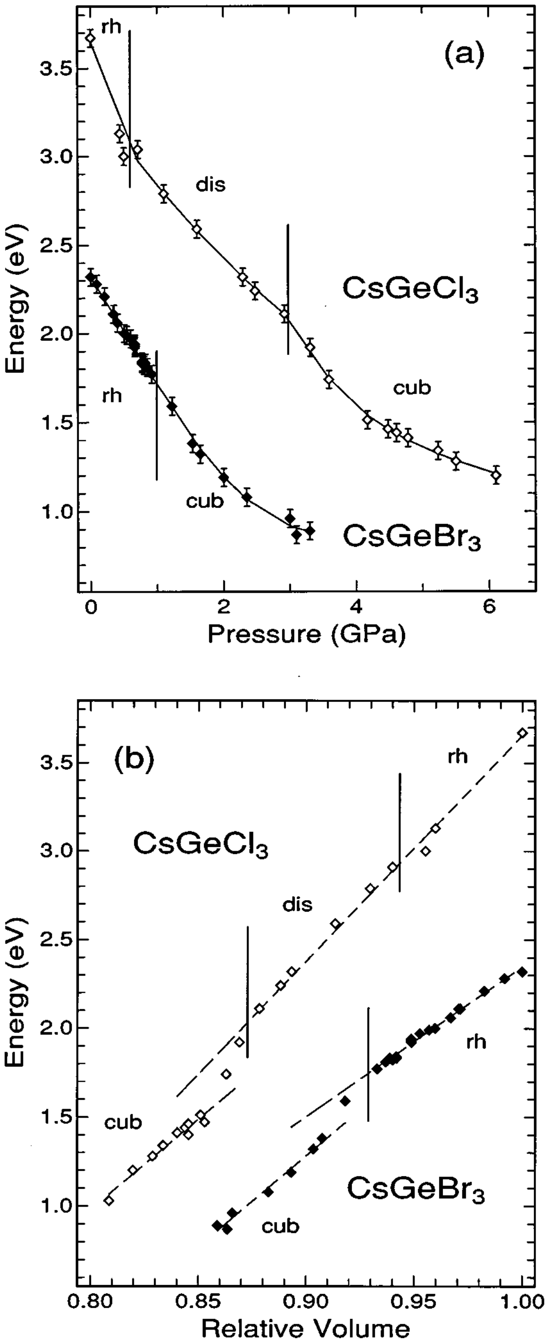

FIG. 3. Absorption edge energies of $CsGeBr_3$ and $CsGeCl_3$ as a function of (a) pressure and (b) relative volume. Phase transition pressures between rhombohedral (rh), cubic disordered (dis), and cubic primitive (cub) phases are indicated by vertical lines. Solid lines drawn through the data points in (a) are guides to the eye. The slopes of the dashed lines in (b) correspond to the average deformation potentials given in the text. Error bars in (a) are estimated uncertainties involved in the determination of the absorption edge energies.

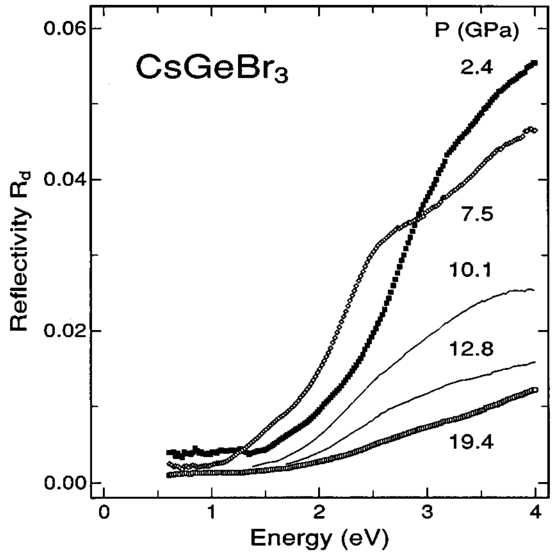

FIG. 4. Optical-reflectivity spectra of $CsGeBr_3$ at different pressures. Absolute reflectivity values refer to the interface between diamond window and sample.

formed within Hartree-Fock theory using the CRYSTAL 92 program.[13] Based on earlier calculations of ground state properties,[6] we chose the pseudopotential/Gaussian-type orbital (GTO) valence–basis-set combination that yields the best description of the structural properties. It consists of a nine-valence-electron pseudopotential and a $(5s5p1d))/[3s3p1d]$ basis for Cs, and a four- and seven-valence-electron pseudopotential for Ge and Br using a $(4s4p1d)/[2s2p1d]$ basis for each. From more accurate molecular calculations we could show that the error of about 6% in the optimized lattice constants for the cubic and the rhombohedral phases is mainly due to neglect of core-valence correlation for the Cs atom. Since Cs-atom contributions do not play an important role in the fundamental gap formation in $CsGeBr_3$ we have performed the band calculations at the experimental lattice constants. It is well known that the absolute value of the splitting between the highest occupied and lowest unoccupied molecular orbitals (HOMO-LUMO) (band gap) on the simple Hartree-Fock level is always too large. Nevertheless, the calculated gap deformation potential D can be expected to be within a reasonable range of the experimental result since partial error cancellation is expected.

Figure 5 shows the band dispersion for the simple cubic structure at the volume corresponding to the phase transition pressure (lattice constant 549 pm). The band structure looks qualitatively similar to the one obtained by Bose *et al.*[3] for isostructural $CsSnBr_3$ using the linear muffin-tin orbitals atomic-sphere approximation (LMTO-ASA) method. A completely flat Cs$(5p)$ band at around -17 eV appears in our band structure, which was treated as a core state in their

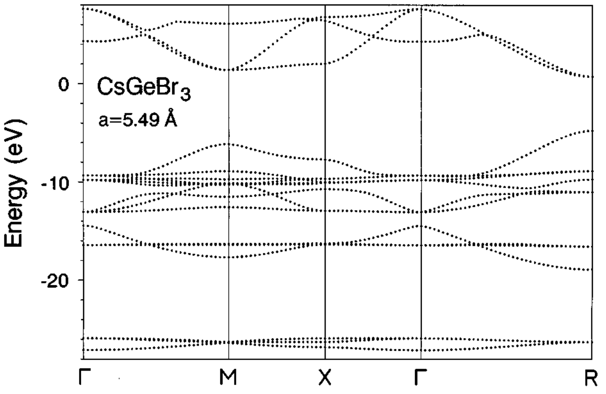

FIG. 5. Hartree-Fock band structure of the cubic primitive modification of $CsGeBr_3$ calculated for the volume at the pressure-induced phase transition near 1 GPa.

calculations. In the same energy region lies the more dispersive nominal Ge(4s) band, which hybridizes with the Br (4p) bands. The Ge(4s)-Br(4p) bonding character increases in the sequence Γ, X, M, R, and the Ge(4s) band energy decreases correspondingly. The next nine occupied bands are the nominal Br(4p) bands. The highest of them is the corresponding Ge(4s)-Br(4p) antibonding partner to the nominal Ge(4s) band and its energy therefore increases in the sequence Γ, X, M, R. Consequently, the top of the upper valence band is located at point R. In the notation of Bouckaert-Smoluchowski-Wigner[14] its symmetry can be labeled as R_1.[15]

The following three unoccupied bands are the nominal Ge (4p) bands. The resulting triply degenerate level at R has R_{15} symmetry and may therefore mix with Br(4s) contributions. This is indeed the case in our calculations, and the admixture is Ge(4p)-Br(4s) antibonding. As a result, we obtain the band structure of a direct gap semiconductor with the smallest gap being located at point R. Since the transition R_1-R_{15} involves the excitation from mixed Ge(s)Br(p) to Ge(p)Br(s) states it is dipole allowed. Thus, contrary to the assignment of Lefebvre *et al.*[16] for $CsSnBr_3$, we attribute the lowest optical excitation to the direct R_1-R_{15} transition.

Calculations have been performed for the cubic structure at several lattice constants. For symmetry reasons, it is expected that bands with pure Ge(4p) character at point R would shift towards lower energy with decreasing volume. However, despite the large energy difference between the nominal Ge(4p) and Br(4s) states, the interaction is sufficiently large to prevent this band from decreasing in energy with increasing pressures. Thus both the R_1 and the R_{15} states increase in energy as the volume is reduced, but the effect is stronger for the R_1 state. Therefore the energy gap is reduced with decreasing volume. The calculated redshift is slightly nonlinear in volume (calculated gap energies are 5.82, 5.50, 5.02, and 4.52 eV at $V/V_0 = 1$, 0.947, 0.897, and 0.848, respectively). The corresponding average gap deformation potential of 8.7 eV is in good agreement with the average experimental values.

In conclusion, optical-absorption spectra show that the fundamental optical gap of $CsGeBr_3$ decreases at an extremely large rate of -0.61 eV/GPa during initial compression. The redshift is nearly continuous at the phase transition to the simple cubic high-pressure polymorph at 1 GPa. Band structure calculations within the Hartree-Fock formalism (simple cubic structure) show that the upper valence bands are formed from Br(4p) states which hybridize strongly with Ge(4s) bands. The lowest conduction bands are formed from Ge(4p) and Br(4s) states. In first approximation, the direct fundamental gap at the R point of the Brillouin zone corresponds to an excitation from antibonding Ge(4s)/Br (4p) states to Ge(4p)/Br(4s) states with antibonding character. The calculated gap deformation potential of 8.7 eV is in good agreement with experimental values. The absorption edge of $CsGeCl_3$ also is very sensitive to pressure, decreasing by about 2.5 eV in a pressure range up to 6 GPa. Despite the large redshift of the absorption edge under pressure, optical reflectivity shows no evidence for metallization below 30 GPa in $CsGeBr_3$.

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