Nonlinear pressure dependence of the direct band gap in adamantine ordered-vacancy compounds

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A strong nonlinear pressure dependence of the optical absorption edge has been measured in defect chalcopyrites $CdGa_2Se_4$ and $HgGa_2Se_4$. The behavior is due to the nonlinear pressure dependence of the direct band-gap energy in these compounds as confirmed by *ab initio* calculations. Our calculations for $CdGa_2Se_4$, $HgGa_2Se_4$ and monoclinic β-Ga_2Se_3 provide evidence that the nonlinear pressure dependence of the direct band-gap energy is a general feature of adamantine ordered-vacancy compounds irrespective of their composition and crystalline structure. The nonlinear behavior is due to a conduction band anticrossing at the Γ point of the Brillouin zone caused by the presence of ordered vacancies in the unit cell of these tetrahedrally coordinated compounds.

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I. INTRODUCTION

Adamantine compounds are tetrahedrally coordinated materials whose structure derives from the cubic diamond structure. They include binary zincblende compounds and their alloys and ternary compounds like chalcopyrite, stannite, and famatinite. A different kind of adamantine compounds are ordered-vacancy compounds (OVCs), in which a cationic site at the unit cell is vacant in an ordered and stoichiometric fashion. Adamantine OVCs include binary $B_2^{III}X_3^{VI}$ and ternary $A^{II}B_2^{III}X_4^{VI}$ compounds, in which one third and one fourth of the cation sites are vacant, respectively. OVCs crystallize in noncubic structures because the presence of several nonequivalent tetrahedrally coordinated cations produces a distortion of the crystal lattice from the cubic symmetry. The lack of cubic symmetry of OVCs provides them with special properties with important applications in optoelectronics, solar cells, and nonlinear optics that have attracted considerable attention.[1–3] Furthermore, they are important materials in solid state physics and defect engineering from a fundamental point of view because they can help to understand the role played by vacancies in the physical and chemical properties of solids. Note that OVCs constitute a bridge between common materials (with vacancies as point or line defects) and amorphous or defect materials (with vacancies and other defects preventing long-range order).

Ternary $A^{II}B_2^{III}X_4^{VI}$ compounds crystallize in the defect chalcopyrite (DC, $I\bar{4}$), defect stannite (DS, $I\bar{4}2m$), or pseudocubic (PS, $P\bar{4}2m$) structures.[1,2] Figure 1(a) shows the tetragonal DC structure of cadmium digallium selenide ($CdGa_2Se_4$) whose atoms (Wyckoff site) are Ga (2a), vacancy (2b), Ga (2c), Cd (2d), and Se (8g) and Fig. 1(b) shows the pseudocubic PS structure of $CdGa_2Se_4$. Theoretical calculations of the optical band-gap energies at different pressures in some ternary OVCs with DC structure have been reported;[3–5] however, only a couple of measurements on the pressure dependence of the optical absorption in OVCs [DC-$MnGa_2Se_4$ (Ref. 6) and monoclinic β-Ga_2Se_3 (Ref. 7)] have been reported. In this work, we report high-pressure optical absorption measurements in DC-$CdGa_2Se_4$ and DC-$HgGa_2Se_4$ and first-principles calculations of the electronic structure for these compounds, and for β-Ga_2Se_3 whose monoclinic Cc structure is shown in Fig. 1(c). We will show that adamatine OVCs exhibit strikingly large absolute deformation potentials for the valence and conduction bands, which are up to 10 times larger than those in tetrahedral semiconductors with zincblende or wurtzite structures. Furthermore, we will show that they have a strong nonlinear pressure dependence of the direct band gap caused by: (i) a large pressure coefficient of the topmost valence band (VB), and (ii) a band anticrossing of the two lowermost conduction bands (CBs) at high pressure.

II. EXPERIMENTAL DETAILS

Stoichiometric single crystals of DC-$CdGa_2Se_4$ (DC-$HgGa_2Se_4$) around 20 μm in thickness and grown from its constituents CdSe (HgSe) and Ga_2Se_3 by chemical vapor

