High-pressure optical and vibrational properties of $CdGa_2Se_4$: Order-disorder processes in adamantine compounds

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High-pressure optical absorption and Raman scattering measurements have been performed in defect chalcopyrite (DC) $CdGa_2Se_4$ up to 22 GPa during two pressure cycles to investigate the pressure-induced order-disorder phase transitions taking place in this ordered-vacancy compound. Our measurements reveal that on decreasing pressure from 22 GPa, the sample does not revert to the initial phase but likely to a disordered zinc blende (DZ) structure the direct bandgap and Raman-active modes of which have been measured during a second upstroke. Our measurements have been complemented with electronic structure and lattice dynamical *ab initio* calculations. Lattice dynamical calculations have helped us to discuss and assign the symmetries of the Raman modes of the DC phase. Additionally, our electronic band structure calculations have helped us in discussing the order-disorder effects taking place above 6–8 GPa during the first upstroke. © *2012 American Institute of Physics*. [doi:10.1063/1.3675162]

I. INTRODUCTION

Adamantine ordered-vacancy compounds (OVCs) constitute a class of compounds derived from the diamond or zinc blende structure with a different number of anions and cations and in which a cation site is vacant in an ordered and stoichiometric fashion. They are tetrahedrally coordinated compounds and include binary B_2X_3 compounds, like sesquisulfides and sesquiselenides, and ternary AB_2X_4 compounds. These latter compounds typically crystallize in one of three tetragonal structures: (i) the defect chalcopyrite (DC) structure with space group (S.G.) I-4, No. 82 [see Fig. 1(a)], (ii) the defect stannite (DS) structure with S.G. I-42 m, No. 121 [also known as defect famatinite, see Fig. 1(b)], and (iii) the pseudocubic (PS) structure (S.G. P-42 m, No. 111).

Despite their different structures, adamantine ternary compounds have in common, unlike in the zinc blende structure, the presence of several nonequivalent tetrahedrally coordinated cations. Consequently, the doubling of the cubic zinc blende unit cell along the *c* axis in these compounds results in a tetragonal symmetry that provides them with special properties not present in cubic zinc blende-type compounds. In particular, adamantine OVCs have important applications in optoelectronics, solar cells, and non-linear optics that have attracted considerable attention in the last 30 years as evidenced in several reviews.[1–4] In this sense, cadmium digallium selenide ($CdGa_2Se_4$) has considerable interest for optoelectronic applications. These semiconductors have potential applications in the field of non-linear optics,[2] photovoltaics,[5] and in diluted magnetic semiconductors.[6] OVCs are used as gyrotropic media in narrow-band optical filters, and in particular $CdGa_2Se_4$ has already found practical applications as a tunable filter and ultraviolet photodetector.[7,8] In addition, this compound is a promising optoelectronic material due to its high values of nonlinear susceptibility, optical activity, intense luminescence, and high photosensitivity.[2]

$CdGa_2Se_4$ is an OVC of the $A^{II}B_2^{III}X_4^{VI}$ family that crystallizes in the tetragonal DC structure[9,10] as depicted in Fig. 1(a), where Ga atoms occupy *2a* and *2c* sites, Cd atoms occupy *2d* sites, vacancies occupy *2b* sites, and Se atoms occupy *8g* sites. $CdGa_2Se_4$ is one of the most studied adamantine ternary compounds, and the behavior of DC-$CdGa_2Se_4$ under pressure has been subject of recent studies.[11–16] In particular, two Raman scattering measurements under pressure[11,12] found a phase transition near 20 GPa to the disordered rock salt (DR) structure [see Fig. 1(c)]. These two studies provided two different symmetry assignments of the Raman-active modes of the DC phase that were not discussed in the latter study despite their use of a Keating-Harrison model.[12] However, both studies agreed on the existence of two stages of cation disorder prior to the phase transition to

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