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Vibrational properties of $CdGa_2S_4$ at high pressure

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ABSTRACT

Raman scattering measurements have been performed in cadmium digallium sulphide ($CdGa_2S_4$) with defect chalcopyrite structure up to 25 GPa in order to study its pressure-induced phase transitions. These measurements have been complemented and compared with lattice-dynamics *ab initio* calculations including the TO-LO splitting at high pressures in order to provide a better assignment of experimental Raman modes. In addition, experimental and theoretical Grüneisen parameters have been reported in order to calculate the molar heat capacity and thermal expansion coefficient of $CdGa_2S_4$. Our measurements provide evidence that $CdGa_2S_4$ undergoes an irreversible phase transition above 15 GPa to a Raman-inactive phase, likely with a disordered rock salt structure. Moreover, the Raman spectrum observed on downstroke from 25 GPa to 2 GPa has been attributed to a new phase, tentatively identified as a disordered zinc blende structure, that undergoes a reversible phase transition to the Raman-inactive phase above 10 GPa.

I. INTRODUCTION

$A^{II}B_2^{III}X_4^{VI}$ compounds are distorted tetrahedrally-coordinated compounds characterized by the presence of stoichiometric vacancies in the unit cell. Vacancies are needed to obey the Grimm-Sommerfeld rule and maintain the charge neutrality, as in other tetrahedrally-coordinated structures derived from the diamond structure.[1] $A^{II}B_2^{III}X_4^{VI}$ compounds are also known as ordered-vacancy compounds (OVCs) and they represent a clear intermediate stage between perfect crystals and amorphous materials. In particular, $CdGa_2S_4$ crystallizes in the defect chalcopyrite (DC) structure [space group (s.g.) $I\bar{4}$, No. 82, $Z = 2$]. Its unit cell can be visualized by doubling the zinc blende (ZB) one (s.g. $F\bar{4}3m$, No. 216, $Z = 4$) of an AX compound along the c-axis and replacing four equal cations of the ZB structure by one Cd cation, two Ga cations, and one vacancy [Fig. 1(a)].

The presence of vacancies in OVCs yields relevant properties in comparison with their homologue AX, BX, and ABX_2 compounds, like higher compressibilities,[2–4] good performance as host materials[5,6] and suitable valence electron concentration, large second harmonic generation, and extensive damage threshold for mid-IR nonlinear optics.[7,8] The most remarkable fields of application of OVCs, due to their wide bandgap, high photosensitivity, bright photoluminescence, and long-term stability of many parameters are photovoltaic cells,[9] optoelectronic devices,[10] temperature sensors,[11] and optical filters.[12,13] In particular, $CdGa_2S_4$ has raised considerable attention in the field of nonlinear optics.[12–14]

Several high-pressure (HP) studies of the properties of OVCs have been reported in the last few years. A combination of multiple experimental techniques such as X-ray diffraction (XRD), Raman