

Comment on “Spectroscopic Signatures of Novel Oxygen-Defect Complexes in Stoichiometrically Controlled CdSe”

In a recent Letter [1] Chen *et al.* reported two groups of local vibrational modes (LVMs) observed in CdSe by infrared measurements. The first group consists of two modes, i.e., $\mu_1 = 1991.77 \text{ cm}^{-1}$ and $\mu_2 = 2001.3 \text{ cm}^{-1}$, which they assigned to oxygen on the Cd site (O_{Cd}). The second group consists of three modes, i.e., $\gamma_1 = 1094.11 \text{ cm}^{-1}$, $\gamma_2 = 1107.45 \text{ cm}^{-1}$, and $\gamma_3 = 1126.33 \text{ cm}^{-1}$, which they assigned to oxygen on the Se site (O_{Se}) in the vicinity of a Cd vacancy (V_{Cd}). For comparison the highest phonon frequencies in corundum Al_2O_3 —one of the hardest known oxides—are below 900 cm^{-1} [2]. The assignment of these LVMs to O implies effective bond stiffness ~ 5 times higher than in Al_2O_3 . Diamond with its exceptionally strong bonding and lighter atoms does not show phonons above 1350 cm^{-1} , and even the bond-stretching mode of the double covalently bonded O_2 molecule is below 1600 cm^{-1} . Frequencies above 2000 cm^{-1} are rare in solid-state compounds with the exception of covalently bonded hydrides. Here we explicitly show that these mode assignments are incorrect and suggest that the observed LVMs are related to hydrogen rather than oxygen based on detailed density functional calculations in the local density approximation. We used a plane-wave basis with cutoff energy of 400 eV and a 96-atom wurtzite supercell.

Our calculations show that O_{Cd} is located off center, binding one axial (along the c axis) and one nonaxial Se atom. The calculated LVMs for O_{Cd} are 389, 342, and 197 cm^{-1} , far lower than 2000 cm^{-1} . Furthermore, O_{Cd} is unstable against interchange of O and a neighboring Se. This results in $O_{\text{Se}}\text{-Se}_{\text{Cd}}$ (a complex of substitutional O on Se site and a Se antisite). Swapping the O and the axial Se lowers the energy by 0.96 eV for the neutral charge state of the defect complex. The neutral Se_{Cd} is also off center due to the Jahn-Teller distortion similar to Te_{Cd} in CdTe as discussed previously [3]. The calculated O LVMs in $O_{\text{Se}}\text{-Se}_{\text{Cd}}$ complex are 411, 392, and 209 cm^{-1} .

The calculated LVMs for an isolated O_{Se} are $\sim 360 \text{ cm}^{-1}$, close to the calculated (341 cm^{-1}) and measured (350 cm^{-1}) [4] LVMs for O_{Te} in CdTe. With a V_{Cd} next to O_{Se} , we find that the nonaxial V_{Cd} is more stable than the axial by only 5 meV. The O_{Se} relaxes away from the vacancy and is nearly on the basal plane of three Cd atoms. The calculated LVMs for the $O_{\text{Se}}\text{-}V_{\text{Cd}}$ (nonaxial) are 495, 494, and 201 cm^{-1} . The two higher LVMs are from in-plane vibrations and the lower LVM is from the out-of-plane vibration. These results are close to the calculated O LVMs for $O_{\text{Te}}\text{-}V_{\text{Cd}}$ in CdTe, i.e., 475 cm^{-1} (double degenerate) and 196 cm^{-1} . A modest increase in

the O_{Se} in-plane LVMs due to the nearby V_{Cd} as we find is reasonable since the Cd-O bond is slightly shortened. Chen *et al.* estimate the LVM for O_{Se} to be $350\text{--}450 \text{ cm}^{-1}$, but assign three LVMs near 1100 cm^{-1} to $O_{\text{Se}}\text{-}V_{\text{Cd}}$. This would imply that a nearby V_{Cd} can increase the O_{Se} LVMs by nearly a factor of 3, i.e., increase the Cd-O bond strength by nearly an order of magnitude, which is unlikely.

Covalently bonded H (e.g., Se-H) is a natural candidate for LVMs of $\sim 2000 \text{ cm}^{-1}$. We calculated the H LVMs for H in V_{Cd} . H can bind with either the axial or nonaxial Se atom. The former is more stable by an insignificant 3 meV. Thus, both H structures should exist. The calculated LVMs for the two H structures are 2092 cm^{-1} (nonaxial) and 2101 cm^{-1} (axial), which are in good agreement with the measured LVMs μ_1 and μ_2 . Since H in the Cd vacancy has nearly equal probability to bind with any of the four surrounding Se atoms, its host isotope fine structure should resemble that of a substitutional cation. This may explain the observation in Ref. [1] that the host isotope fine structures for μ_1 and μ_2 are similar to Mg_{Cd} in CdSe.

The three measured LVMs near 1100 cm^{-1} , γ_1 , γ_2 , and γ_3 , are very close to the two LVMs found in CdTe [4]. This suggests that these LVMs may be related to a common impurity in CdSe and CdTe. Although we have not found a satisfactory model for these LVMs, we suspect that they are related to H. The O-H wagging modes possibly explain the two LVMs near 1100 cm^{-1} in CdTe [3]. It will be helpful to have more experimental information on the impurity and defect characterization to unambiguously answer this remaining question.

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