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Growth of single crystals of CdSe with oxygen, introduced by stoichiometric control to suppress the formation of native Se and Cd vacancies, generates oxygen centers replacing Cd (O_Cd) rather than Se (O_Se) as expected. This antisite substitution is unambiguously singled out by the host isotope fine structure of the nearest neighbor (NN) Se atoms in the localized vibrational modes (LVMs) of O_Cd. When the stoichiometry control favors the formation of Cd vacancies, three infrared signatures \( \gamma_1, \gamma_2 \) and \( \gamma_3 \) appear ascribable to the LVMs of O_Se in association with a Cd vacancy in the NN position as \( (\text{O}_\text{Se} - \text{V}_\text{Cd}) \) centers. Polarization measurements establish the monoclinic \( C_v \) symmetry for these centers. As a function of temperature, they display a remarkable two-step symmetry transformation, \( C_v \rightarrow C_{3v} \rightarrow T_d \), due to the dynamic switching of the \( \text{O}_\text{Se} - \text{V}_\text{Cd} \) dangling bond.


In compound semiconductors, unlike in the elemental, stoichiometry needs to be strictly controlled in order to achieve crystal growth free from imperfections such as cation or anion vacancies, interstitials and antisite substitutions. This is often a prerequisite for the deliberate incorporation of specific impurities in desired concentrations. Native defects often behave like donors or acceptors; Cd vacancies in CdTe and Se vacancies in CdSe [1,2] are reported to be acceptors and donors, respectively. Under certain circumstances a light substitutional impurity in association with the vacancy displays unique infrared signatures characteristic of localized vibrational modes (LVMs). We recently reported [2] such LVMs of oxygen impurities in CdTe in which oxygen substitutionally replaced a tellurium host atom \( \text{O}_{\text{Te}} \), the nearest neighbors (NN) then being the four Cd atoms as \( \text{O}_{\text{Te}} \), or in association with a Cd vacancy in one of the NN sites as \( (\text{O}_{\text{Te}} - \text{V}_\text{Cd}) \). The former has \( T_d \) site symmetry with a single triply degenerate LVM whereas the latter displays two LVMs consistent with its \( C_{3v} \) symmetry [3]. The striking temperature behavior of the doublet in which the two components approached and coalesced showed that the \( (\text{O}_{\text{Te}} - \text{V}_\text{Cd}) \) dangling bond switched its [111] orientation among the four (111) directions and the \( (\text{O}_{\text{Te}} - \text{V}_\text{Cd}) \) complex thus acquired a temperature averaged \( T_d \) symmetry above \( T^* \), the temperature of coalescence.

In order to discover additional examples of such an extraordinary behavior, we have investigated CdSe, with Cd's bonded to Se's and Se's to Cd's in a tetrahedral coordination resulting in a wurtzite crystal with \( C_{6v} \) space group symmetry. By controlling the stoichiometry, our aim was to suppress the native Se vacancies and encourage the formation of O_Se centers tetrahedrally bonded to Cd's in NN positions; such O_Se centers would have \( C_{3v} \) symmetry. However, the incorporation of excess Se in a concentration in excess of that of the native Se vacancies would result in Cd vacancies and \( (\text{O}_\text{Se} - \text{V}_\text{Cd}) \) centers. Crystals of CdSe were grown with these strategies. In this Letter we report the surprising nature of the oxygen related LVMs in CdSe discovered in a high resolution study using Fourier transform spectrometer.

The absorption spectra were recorded using an ultrahigh resolution BOMEM DA.3 Fourier transform infrared (FTIR) spectrometer capable of an ultimate unapodized resolution of 0.0026 cm\(^{-1}\). A HgCdTe-infrared detector for the 500–5000 cm\(^{-1}\) range and an InSb detector for 1800–8500 cm\(^{-1}\) range were employed. A Janis 10DT Supervaritemp continuous-flow optical cryostat allowed measurements in the range of 1.8–300 K and a specially designed high temperature cell in the range of 300–600 K. The orientation of the uniaxial crystals was determined by the Laue back-reflection method. A wire grid polarizer on an AgBr substrate was used in the measurements requiring polarized radiation.

Single crystal of CdSe was grown with the addition of CdO to provide oxygen and excess Se to suppress the occurrence of Se vacancies [4,5]. The infrared spectrum of CdSe prepared in this manner displays two LVMs \( \mu_1 \) and \( \mu_2 \) centered at 1991.77 cm\(^{-1}\) and 2001.3 cm\(^{-1}\) respectively, when recorded at a relatively low resolution and unpolarized incident light. Because of the uniaxial nature of the host crystal, a substitutional impurity is expected to display a local symmetry of \( C_{3v} \), hence two infrared active LVMs, one polarized parallel to \( \hat{c} \), the optic axis and the other \( \perp \hat{c} \). Under the high resolution employed in Fig. 1, both \( \mu_1 \) and \( \mu_2 \) display a remarkable host isotope fine structure strikingly similar to that for MgCd in CdSe [6]. As it is dominated by the natural isotope abundance and the atomic masses of the NN atoms, the host isotope fine structure bears unmistakable similarity for different impurities with the same nearest neighbors in the same host [7,8]. Has oxygen replaced Cd as O_Cd rather than Se as...
$O_{Se}$? In the former case, the fine structure and its similarity with $Mg_{Cd}$ can be explained, since in both cases, the fine structure is associated with NN Se atoms set in vibratory motion by the LVMs of $O_{Cd}$ or $Mg_{Cd}$. Therefore $O_{Cd}$ as an antisite replacement is the clear but surprising choice based on these experimental observations. The large frequencies of $\mu_1$ and $\mu_2$ are yet another indication that oxygen has entered CdSe, replacing Cd as an antisite impurity, not Se as an isoelectronic impurity. If oxygen replaces Se, the LVMs of $O_{Se}$ are expected in the spectral range of 350–450 cm$^{-1}$ from the knowledge of the LVMs of $S_{Se}$ in CdSe [9]. When measured with a Si bolometer which covers this spectral range, no evidence for $O_{Se}$ was found. The large frequencies can well be attributed to four extra electrons surrounding the $O_{Cd}$ center which significantly increase the effective force constants responsible for $\mu_1$ and $\mu_2$. The observation of a single pair of $\mu_1$ and $\mu_2$, and its intensity proportional to the CdO added to the starting material during crystal growth, rules out $Se_{Cd}$ instead of $O_{Cd}$ being the cause for $\mu_1$ and $\mu_2$.

Experiments with incident radiation polarized parallel to the $\hat{c}$ axis, $E \parallel \hat{c}$, $\mu_1$ reduced dramatically as compared to $\mu_2$, whereas for radiation polarized perpendicular to the $\hat{c}$ axis, $E \perp \hat{c}$, $\mu_1$ also decreased to zero. On the basis of these polarization measurements, we assign $\mu_1$ to the localized vibration parallel to the $\hat{c}$ axis and $\mu_2$ to vibration perpendicular to $\hat{c}$ as indicated in Fig. 1.

In the samples of CdSe grown with CdO to provide oxygen and an additional large amount of Se not only to suppress the existing Se vacancies but also to produce Cd vacancies, three absorption peaks are observed at $\gamma_1 = 1094.11$ cm$^{-1}$, $\gamma_2 = 1107.45$ cm$^{-1}$, $\gamma_3 = 1126.33$ cm$^{-1}$ without $\mu_1$ and $\mu_2$ appearing. We propose that in these samples oxygen substitutionally replaces Se ($O_{Se}$) in the vicinity of a Cd vacancy ($V_{Cd}$). Because the host crystal has wurtzite structure, the NN vacancy along $\hat{c}$ is different from those at one of the other three sites. In the former configuration, the ($O_{Se} - V_{Cd}$) center has $C_{3v}$ symmetry and will display two infrared active modes, one along $\hat{c}$ and the other, perpendicular to the $\hat{c}$ axis. A Cd vacancy can also occupy any one of the three NN sites in the plane normal to $\hat{c}$ which are characterized by a dangling bond not parallel to the $\hat{c}$ axis; such ($O_{Se} - V_{Cd}$) centers have a $C_s$ local symmetry and should exhibit three infrared active modes. Since three infrared active modes are observed experimentally, we choose $C_{3v}$ symmetry for the ($O_{Se} - V_{Cd}$) centers hence the atomic configuration shown in Fig. 2.

Consider the symmetry of an ($O_{Se} - V_{Cd}$) center shown in Fig. 2. It has a plane of reflection which contains a Cd atom in position 1, an oxygen impurity ($O_{Se}$) and a Cd vacancy (in this case, at position 3). In two of the three infrared active modes $O_{Se}$ will vibrate in the plane of symmetry ($\sigma$ plane) as indicated in Fig. 2, while in the third it will vibrate perpendicular to the $\sigma$ plane hence perpendicular to the $\hat{c}$ axis [10]. Thus $\gamma_1$, $\gamma_2$, and $\gamma_3$ will be polarized along three directions, two in the $\sigma$ plane and the third $\perp \sigma$.
Given the (OSe – V_{Cd}) center with its C\textsubscript{3} symmetry, the intensities of \(\gamma_1\), \(\gamma_2\), and \(\gamma_3\) differ from one to another. The different (OSe – V_{Cd}) centers will all have “Cd-O” axes parallel to \(\hat{c}\) but their \(\sigma\)-planes defined by \(\mathbf{R}(\gamma_2)\) at 120° with respect to one another, distributed randomly over the crystal. Distributed into three equal populations of defect orientations defined by the Cd vacancy in positions 2, 3, or 4, the \(\gamma\)’s will display a corresponding “orientational” degeneracy [11]. Therefore, averaged over the crystal as a whole, \(\gamma_1\), \(\gamma_2\), and \(\gamma_3\) will display isotropy when viewed along \(\hat{c}\). This effect is directly demonstrated by the indistinguishable absorption spectra recorded with radiation incident along \(\hat{c}\) and polarized along two mutually orthogonal arbitrary directions in the plane normal to \(\hat{c}\).

Consider the infrared active mode in which oxygen vibrates perpendicular to the \(\sigma\) plane hence perpendicular to \(\hat{c}\) irrespective of the position of the Cd vacancy. Such a mode is completely polarized for \(\mathbf{E} \perp \hat{c}\), but will not couple to it for \(\mathbf{E} \parallel \hat{c}\). This prediction is directly confirmed as shown in Fig. 3. The \(\gamma_2\) mode becomes extremely weak when the incident light is polarized \(\parallel \hat{c}\), while it is the most intense when the incident light is polarized \(\perp \hat{c}\) (the very small intensities of \(\gamma_2\) for \(\mathbf{E} \parallel \hat{c}\) can be attributed to the finite convergence of the radiation incident on the crystal).

Based on these experimental observations, we assign \(\gamma_2\) to the infrared active mode in which oxygen vibrates \(\perp \hat{c}\). Depending on the angles they make with respect to the \(\hat{c}\) axis, \(\gamma_1\) and \(\gamma_3\) will differ in their intensities for \(\mathbf{E} \parallel \hat{c}\) compared to \(\mathbf{E} \perp \hat{c}\) as shown in Fig. 3.

The temperature dependence of the frequencies of \(\gamma_1\), \(\gamma_2\), and \(\gamma_3\) for the (OSe – V_{Cd}) centers is remarkable. As the temperature increases, they do not change significantly from 5 to 200 K, beyond which, \(\gamma_1\) increases, whereas \(\gamma_2\) and \(\gamma_3\) decrease. As seen in Fig. 4(d), with increasing temperature, \(\gamma_1\) and \(\gamma_2\) approach each other and coalesce into a single, doubly degenerate mode \(\gamma_{12}\) at \(T_1 \sim 480\) K. We propose that a dynamic switching of the OSe – V_{Cd} dangling bond among the three equivalent positions 2, 3, and 4 occurs and transforms the site symmetry of the oxygen-vacancy complex from \(C_s\) to \(C_{3v}\) as the OSe – V_{Cd} bond switching occurs at an increasing rate and the (OSe – V_{Cd}) defect center increasingly acquires \(C_{3v}\) sym-
metry; this acquired symmetry is reflected in the $\gamma_1$ normal mode also to vibrate normal to the $\hat{c}$ axis resulting in a doubly degenerate $\gamma_{12}$ mode of $C_{3v}$ symmetry as schematically shown in Fig. 4(b).

With a further increase in temperature, $\gamma_3$ decreases while $\gamma_{12}$ increases slightly and merges with $\gamma_3$, i.e., to become a single, “triply degenerate” $\gamma_{123}$ mode at $T_2 \sim 560$ K, i.e., at higher temperatures, the “OSe – V\textsubscript{Cd}” dangling bond of the (OSe – V\textsubscript{Cd}) center switches rapidly among all the four Cd positions 1, 2, 3, and 4 with equal probabilities, and the net symmetry of the (OSe – V\textsubscript{Cd}) center effectively transforms into a quasi-$T_d$ site symmetry as schematically represented in Fig. 4(c).

The work reported in this Letter underscores the important role stoichiometry plays in the impurity configurations in compound semiconductors. The antisite replacement of oxygen (O\textsubscript{Cd}) unambiguously revealed in the host isotope fine structure expected for its LVMs, the atomic configuration and site symmetry of (OSe – V\textsubscript{Cd}) centers uniquely revealed by the polarization measurements and a two-step symmetry transformation produced by increasing temperatures, attributed to the dynamic switching of the dangling bond are the highlights of the present work.

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