Spectroscopic Signatures of Novel Oxygen-Defect Complexes in Stoichiometrically Controlled CdSe

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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 γ_1, γ_2 and γ_3 appear ascribable to the LVMs of O_{Se} in association with a Cd vacancy in the NN position as ($O_{Se} - V_{Cd}$) centers. Polarization measurements establish the monoclinic C_s symmetry for these centers. As a function of temperature, they display a remarkable two-step symmetry transformation, $C_s \rightarrow C_{3v} \rightarrow T_d$, due to the dynamic switching of the $O_{Se} - V_{Cd}$ dangling bond.

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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 imputities in CdTe in which oxygen substitutionaly replaced a tellurium host atom (O_{Te}), the nearest neighbors (NN) then being the four Cd atoms as O_{Te}, or in association with a Cd vacancy in one of the NN site as ($O_{Te} - V_{Cd}$). 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 ($O_{Te} - V_{Cd}$) dangling bond switched its [111] orientation among the four ⟨111⟩ directions and the ($O_{Te} - V_{Cd}$) 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}^4 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 ($O_{Se} - V_{Cd}$) 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 a 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 μ_1 and μ_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 μ_1 and μ_2 display a remarkable host isotope fine structure strikingly similar to that for Mg_{Cd} 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

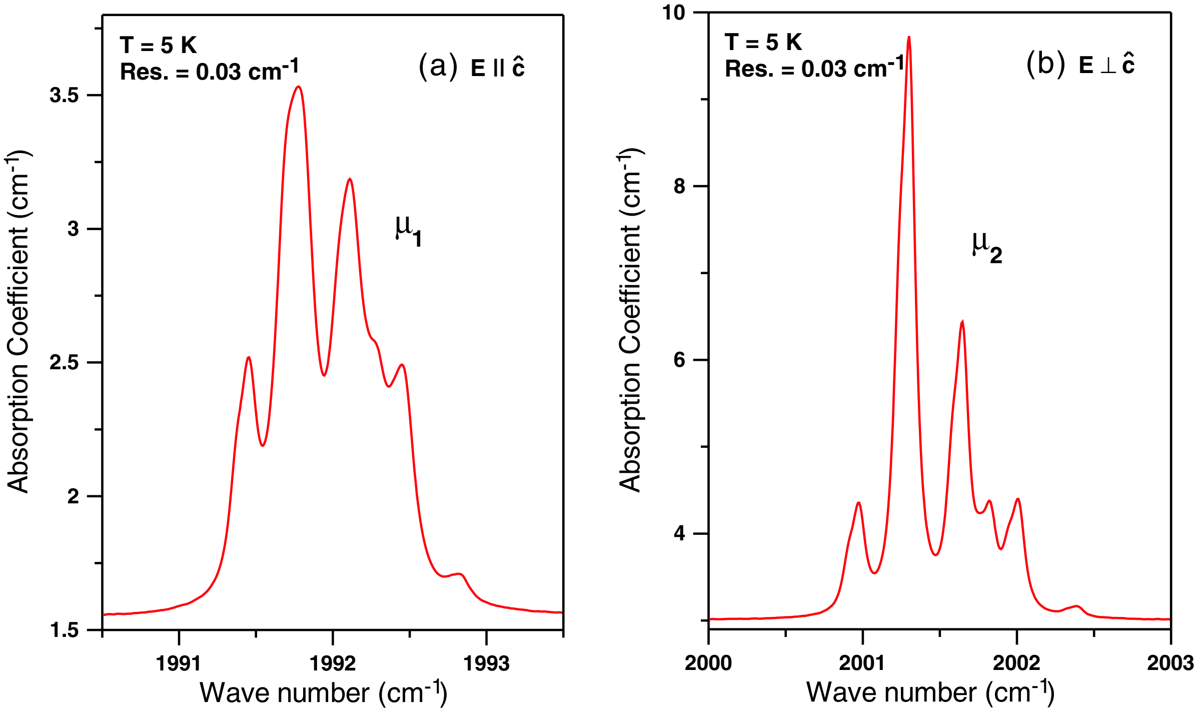

FIG. 1 (color online). The fine structure of the O_{Cd} LVMs in CdSe for (a) **E** ∥ **ĉ** and for (b) **E** ⊥ **ĉ**, where **E** is the electric vector of the incident light and **ĉ**, the optic axis.

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 μ_1 and μ_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 μ_1 and μ_2. The observation of a single pair of μ_1 and μ_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 μ_1 and μ_2.

Experiments with incident radiation polarized parallel to the **ĉ** axis, **E** ∥ **ĉ**, μ_2 reduced dramatically as compared to μ_1, whereas for radiation polarized perpendicular to the **ĉ** axis, **E** ⊥ **ĉ**, μ_1 also decreased to zero. On the basis of these polarization measurements, we assign μ_1 to the localized vibration parallel to the **ĉ** axis and μ_2 to vibration perpendicular to **ĉ** 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 $\gamma_1 = 1094.11\ \mathrm{cm}^{-1}$, $\gamma_2 = 1107.45\ \mathrm{cm}^{-1}$, $\gamma_3 = 1126.33\ \mathrm{cm}^{-1}$ without μ_1 and μ_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 **ĉ** 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 **ĉ** and the other, perpendicular to the **ĉ** axis. A Cd vacancy can also occupy any one of the three NN sites in the plane normal to **ĉ** which are characterized by a dangling bond not parallel to the **ĉ** 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_s 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 (σ plane) as indicated in Fig. 2, while in the third it will vibrate perpendicular to the σ plane hence perpendicular to the **ĉ** axis [10]. Thus γ_1, γ_2, and γ_3 will be polarized along three directions, two in the σ plane and the third ⊥ σ.

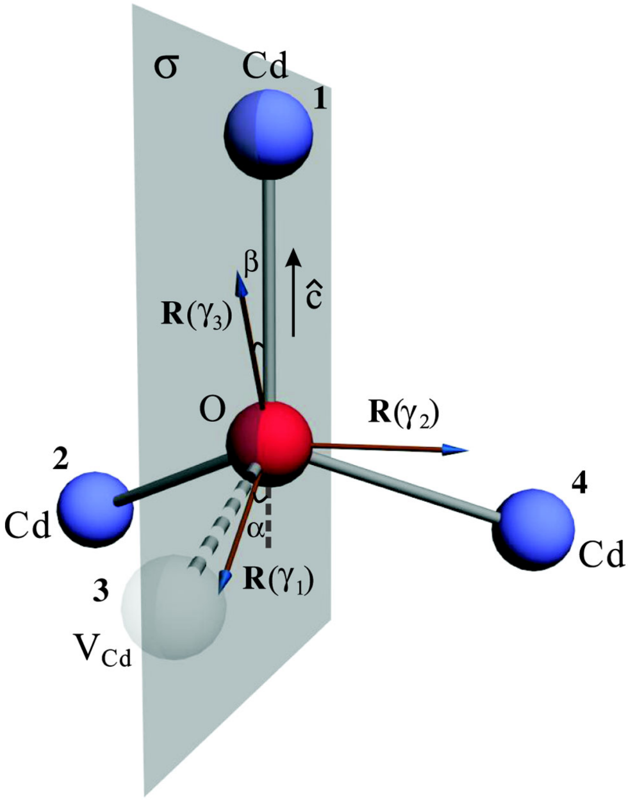

FIG. 2 (color online). A three-dimensional model for the $(O_{Se} - V_{Cd})$ center with Cd vacancy at 3, two of the nearest neighbor Cd atoms at 2 and 4 and third at 1 on $\hat{\mathbf{c}}$. Also shown is the plane of reflection, σ, on which the Cd atom at 1, O_{Se}, and the Cd vacancy at 3 are located. Oxygen vibrations for γ_1 and γ_3 are along $\mathbf{R}(\gamma_1)$ and $\mathbf{R}(\gamma_3)$ lying on σ and $\mathbf{R}(\gamma_2)$ normal to σ. $\mathbf{R}(\gamma_1)$, $\mathbf{R}(\gamma_2)$, and $\mathbf{R}(\gamma_3)$ are mutually perpendicular.

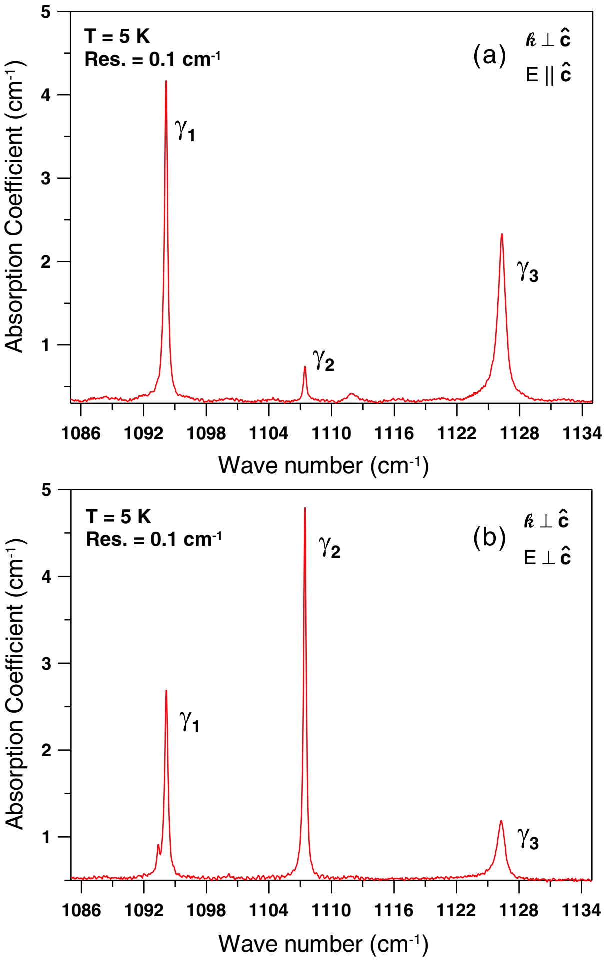

FIG. 3 (color online). The figure shows the polarizations of γ_1, γ_2, and γ_3, with the direction of propagation of the incident radiation, $\mathbf{k}$, perpendicular to $\hat{\mathbf{c}}$, and the electric vector, $\mathbf{E}$, parallel to $\hat{\mathbf{c}}$ in (a) and perpendicular to $\hat{\mathbf{c}}$ in (b).

Given the $(O_{Se} - V_{Cd})$ center with its C_s symmetry, the intensities of γ_1, γ_2, and γ_3 differ from one to another. The different $(O_{Se} - V_{Cd})$ centers will all have "Cd-O" axes parallel to $\hat{\mathbf{c}}$ but their σ-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 position 2, 3, or 4, the γ's will display a corresponding "orientational" degeneracy [11]. Therefore, averaged over the crystal as a whole, γ_1, γ_2, and γ_3 will display isotropy when viewed along $\hat{\mathbf{c}}$. This effect is directly demonstrated by the indistinguishable absorption spectra recorded with radiation incident along $\hat{\mathbf{c}}$ and polarized along two mutually orthogonal arbitrary directions in the plane normal to $\hat{\mathbf{c}}$.

Consider the infrared active mode in which oxygen vibrates perpendicular to the σ plane hence perpendicular to $\hat{\mathbf{c}}$ irrespective of the position of the Cd vacancy. Such a mode is completely polarized for $\mathbf{E} \perp \hat{\mathbf{c}}$, but will not couple to it for $\mathbf{E} \parallel \hat{\mathbf{c}}$. This prediction is directly confirmed as shown in Fig. 3. The γ_2 mode becomes extremely weak when the incident light is polarized $\parallel \hat{\mathbf{c}}$, while it is the most intense when the incident light is polarized $\perp \hat{\mathbf{c}}$ (the very small intensities of γ_2 for $\mathbf{E} \parallel \hat{\mathbf{c}}$ can be attributed to the finite convergence of the radiation incident on the crystal). Based on these experimental observations, we assign γ_2 to the infrared active mode in which oxygen vibrates $\perp \hat{\mathbf{c}}$. Depending on the angles they make with respect to the $\hat{\mathbf{c}}$ axis, γ_1 and γ_3 will differ in their intensities for $\mathbf{E} \parallel \hat{\mathbf{c}}$ compared to $\mathbf{E} \perp \hat{\mathbf{c}}$ as shown in Fig. 3.

The temperature dependence of the frequencies of γ_1, γ_2, and γ_3 for the $(O_{Se} - V_{Cd})$ centers is remarkable. As the temperature increases, they do not change significantly from 5 to 200 K, beyond which, γ_1 increases, whereas γ_2 and γ_3 decrease. As seen in Fig. 4(d), with increasing temperature, γ_1 and γ_2 approach each other and coalesce into a single, doubly degenerate mode γ_{12} at $T_1 \sim 480$ K. We propose that a dynamic switching of the $O_{Se} - V_{Cd}$ 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 $O_{Se} - V_{Cd}$ bond switching occurs at an increasing rate and the $(O_{Se} - V_{Cd})$ defect center increasingly acquires C_{3v} sym-

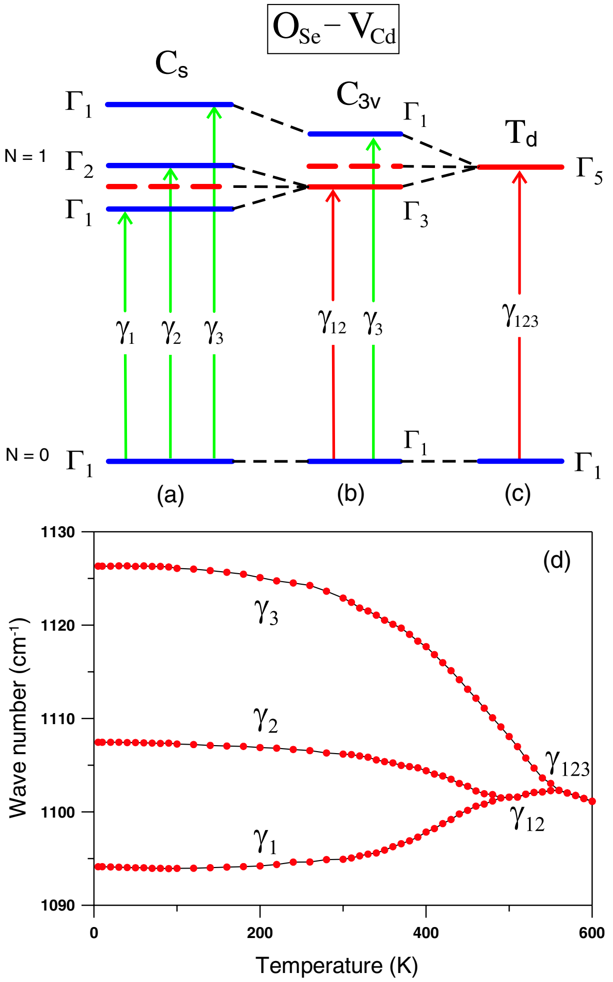

FIG. 4 (color online). Schematic energy level diagrams and the fundamental dipole transitions in (a) ($O_{Se} - V_{Cd}$) center with C_s site symmetry, (b) ($O_{Se} - V_{Cd}$) center with dynamic switching of the dangling bond included and symmetry of the center transforms from C_s to a C_{3v} site symmetry, (c) ($O_{Se} - V_{Cd}$) center with dynamic switching of the dangling bond included and the center acquires a quasi-T_d site symmetry. (d) The temperature dependence of γ_1, γ_2, and γ_3 for the ($O_{Se} - V_{Cd}$) center from 5 to 600 K.

metry; this acquired symmetry is reflected in the γ_1 normal mode also to vibrate normal to the $\hat{\mathbf{c}}$ axis resulting in a doubly degenerate γ_{12} mode of C_{3v} symmetry as schematically shown in Fig. 4(b).

With a further increase in temperature, γ_3 decreases while γ_{12} increases slightly and merges with γ_3, i.e., to become a single, "triply degenerate" γ_{123} mode at $T_2 \sim$ 560 K, i.e., at higher temperatures, the "$O_{Se} - V_{Cd}$" dangling bond of the ($O_{Se} - V_{Cd}$) center switches rapidly among all the four Cd positions 1, 2, 3, and 4 with equal probabilities, and the net symmetry of the ($O_{Se} - V_{Cd}$) 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_{Cd}) unambiguously revealed in the host isotope fine structure expected for its LVMs, the atomic configuration and site symmetry of ($O_{Se} - V_{Cd}$) 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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