

Cadmium vacancy passivated by two hydrogen atoms in CdSe

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Two previously reported local vibrational modes (LVMs) in CdSe single crystals at 1992 and 2001 cm^{-1} [Chen *et al.*, *Phys. Rev. Lett.* **101**, 195502 (2008)] are generated in the present study by annealing the crystals in H_2 gas at 500 °C. The absorption bands shift to 1454 and 1461 cm^{-1} when the samples were annealed in ambient D_2 . Each LVM consists of at least five lines. The relative intensities match the natural abundance of the predominant Se isotopes. The 1992- and 2001- cm^{-1} lines are assigned to two selenium-hydrogen vibrations in the Cd vacancy.

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I. INTRODUCTION

Defect formation in II–VI compounds is strongly influenced by the precise stoichiometry of the crystals. The variation of intrinsic defects allows the incorporation of impurities in more than one configuration. This property of II–VI compounds leads to the formation of compensating defects, which are a strong handicap in shallow donor/acceptor doping but are also a prerequisite for high-resistivity materials.

IR absorption studies on CdSe have led to much information on substitutional defects on the Cd side as well as on the Se side.^{1–5} Recently, Chen *et al.* reported on two high-frequency IR absorption lines, at about 1992 cm^{-1} (μ_1) and 2001 cm^{-1} (μ_2), in CdSe grown with the addition of CdO.⁶ Based on the correlation between the μ -line intensities and the oxygen content, these lines were assigned to the local vibrational modes (LVMs) of substitutional oxygen at the Cd site, O_{Cd} . The assignment O_{Cd} was contested by first principles theory.^{7,8} Thienprasert *et al.* found that LVMs of O_{Cd} have frequencies of 417 and 502 cm^{-1} for the neutral charge state of the defect (O_{Cd}^0) and 158 and 723 cm^{-1} for the double negatively charged state $\text{O}_{\text{Cd}}^{2-}$,⁸ which are significantly lower than the frequencies of the μ modes. Moreover, due to the high formation energy (3 eV), the concentration of O_{Cd} in CdSe should be marginally low.⁸ As the possible origin of μ_1 and μ_2 modes, a Cd vacancy saturated by two hydrogen atoms ($\text{V}_{\text{Cd}}\text{H}_2$) was suggested.⁷

The Cd vacancy in CdSe (V_{Cd}) is a double acceptor whose doubly ionized state gives rise to a level 0.65 eV above the valence band.^{9–13} According to theory, hydrogen can passivate V_{Cd} via the formation of two Se–H bonds aligned either parallel (SeH_{\parallel}) or perpendicular (SeH_{\perp}) to the c axis of the crystal.⁷ The calculated LVMs are 2092 cm^{-1} (SeH_{\parallel}) and 2101 cm^{-1} (SeH_{\perp}), with the SeH_{\parallel} bond being more stable by only 3 meV compared to SeH_{\perp} .

In this report we identify the μ modes as LVMs of two Se–H bonds in the Cd vacancy $\text{V}_{\text{Cd}}\text{H}_2$.

II. EXPERIMENTAL PROCEDURE

The CdSe samples used in this work were high-resistivity, polished, (11 $\bar{2}$ 0)-oriented single crystals grown from the vapor phase at the Institute of Material Science and Technology, Russia. Hydrogen and/or deuterium was introduced via annealing of the samples in sealed quartz ampules filled with 0.5 bar at room temperature of H_2 or/and D_2 gas. The treatments

were performed at 500 °C for 1 h and were terminated by quenching of the ampules to room temperature in water.

IR absorption spectra were recorded with a Bomem DA3.01 Fourier spectrometer equipped with a KBr beamsplitter, a global light source, and a liquid nitrogen-cooled MCT detector. The spectral resolution was 0.1–0.2 cm^{-1} . Measurements were performed in a He exchange-gas cryostat equipped with KRS-5 windows. Polarized light was produced by a wire-grid polarizer with a KRS-5 substrate.

III. RESULTS AND DISCUSSION

Figure 1 shows IR absorption spectra of a CdSe sample after treatment in H_2 at 500 °C. Two bands, previously reported by Chen *et al.*⁶ at around 1992 cm^{-1} (μ_1) and 2001 cm^{-1} (μ_2) are shown. We label these SeH_{\parallel} and SeH_{\perp} , respectively. These bands always occur at the same intensity ratio, which strongly indicates that they originate from the same defect.

An annealing of a CdSe sample in ambient D_2 at 500 °C leads to a redshift of the two features SeH_{\parallel} and SeH_{\perp} . The corresponding IR absorption spectra are shown in Fig. 2. The two bands are located at 1454 and 1461 cm^{-1} and are labeled SeD_{\parallel} and SeD_{\perp} . The frequency ratio of the bands in Figs. 1 and 2 is 1.37, which is characteristic for hydrogen-related vibrational modes. These results are evidence of a hydrogen defect in CdSe. An annealing of the treated samples at 500 °C for 1 h leads to a decrease in these signals below the detection limit.

In order to obtain the direction of the dipole moments of SeH_{\parallel} and SeH_{\perp} , we performed IR measurements with linearly polarized light aligned parallel and perpendicular to the c axis (not shown). The angle φ comprised by the dipole moment and the c axis in the C_{3v} point group can be determined from^{14,15}

$$\varphi = \arctan \sqrt{2I_{\perp}/I_{\parallel}}. \quad (1)$$

Here I_{\perp} and I_{\parallel} are the intensities of the light absorbed for the polarizer orientations perpendicular and parallel to c , respectively. We find that the 1992- cm^{-1} mode (SeH_{\parallel}) is aligned parallel to the c axis, whereas the mode at 2001 cm^{-1} (SeH_{\perp}) forms an angle of $113 \pm 4^\circ$ with the c axis.

As mentioned already, Chen *et al.* assigned the 1992- and 2001- cm^{-1} features to LVMs of substitutional oxygen at the Cd site based on the apparent similarity of the fine structure of the 1992- and 2001- cm^{-1} bands to that of Mg_{Cd} in CdSe.^{4,6} In our opinion, the fine structure of these bands

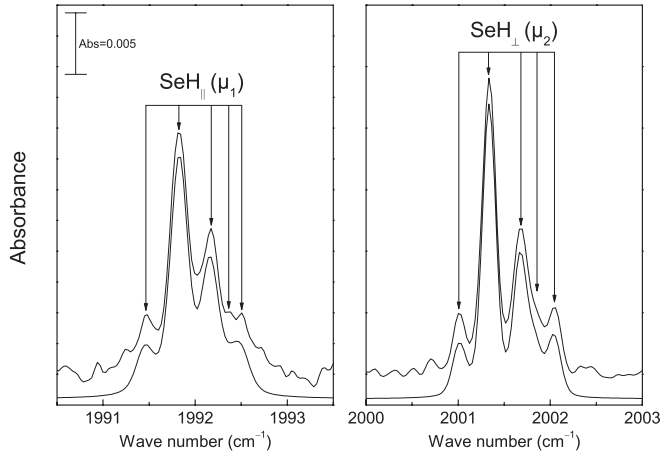


FIG. 1. Upper curve: IR absorption spectra obtained at 8 K from a CdSe sample treated in ambient H₂ at 500 °C. Nonpolarized light. Lower curve: Voigt profile fit consisting of five curves of equal line width.

alone does not support this suggestion. A fit of each band reveals that both features consist of five absorption lines (see Tables I and II), whose relative intensities are independent of the sample history and equal 10:51:27:4:8 (SeH_{||}) and 9:50:23:8:10 (SeH_⊥). The values were obtained by a Voigt profile fit for each absorption line. These intensity ratios are close to the natural abundance of the main five selenium isotopes ⁸²Se : ⁸⁰Se : ⁷⁸Se : ⁷⁷Se : ⁷⁶Se (9:50:24:8:9), which is in favor of the 1992- and 2001-cm⁻¹ bands being due to a single Se atom, rather than a fourfold coordinated substitutional impurity. The relative intensities of SeD_{||} and SeD_⊥ features match the natural abundance of the main Se isotopes as well: 11:47:21:9:12 (SeD_{||}) and 9:46:23:9:13 (SeD_⊥). Therefore, our results rule out a substitutional-type defect. Moreover, if the 1992- and 2001-cm⁻¹ modes were due to the oxygen vibrations, the difference in frequency between the highest and the lowest LVM would be approximately

$$2000 \text{ cm}^{-1} \times \frac{\sqrt{\mu_{^{76}\text{Se}-^{16}\text{O}}} - \sqrt{\mu_{^{82}\text{Se}-^{16}\text{O}}}}{\sqrt{\mu_{^{76}\text{Se}-^{16}\text{O}}}} \approx 13 \text{ cm}^{-1},$$

where $\mu_{^{76}\text{Se}-^{16}\text{O}}$ and $\mu_{^{82}\text{Se}-^{16}\text{O}}$ are the reduced masses of the ⁷⁶Se-¹⁶O and ⁸²Se-¹⁶O units, respectively. On the contrary, the splitting between these LVMs is 1 cm⁻¹, which is close to the expected frequency difference between a ⁷⁶Se-H and

TABLE I. Experimental (Exp.) and best-fit frequencies (in cm⁻¹) obtained with Eqs. (2) and (3) for SeH_{||}. Fitting parameters ω_e , x , and χ refer to ⁷⁸Se and H isotopes.

	⁸² Se	⁸⁰ Se	⁷⁸ Se	⁷⁷ Se	⁷⁶ Se
	SeH				
Exp.	1991.5	1991.8	1992.2	1992.4	1992.5
Fit	1991.6	1991.9	1992.2	1992.3	1992.5
	SeD				
Exp.	1453.9	1454.3	1454.8	1455.0	1455.3
Fit	1454.0	1454.4	1454.8	1455.0	1455.2
$\omega_e = 2170.7$	$x = 0.0411$		$\chi = 1.0182$		

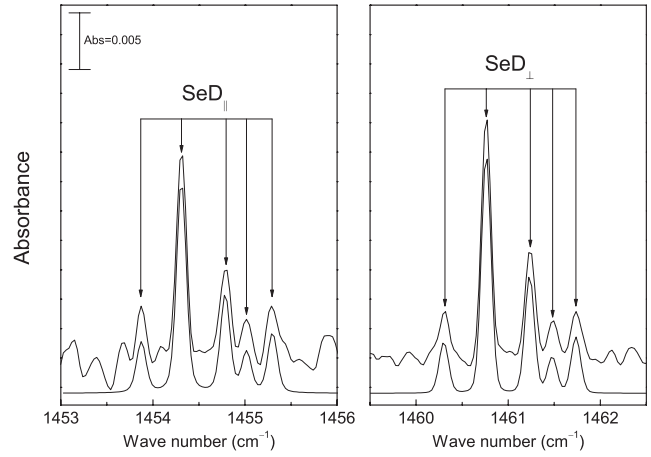


FIG. 2. Upper curve: IR absorption spectra obtained at 8 K from a CdSe sample treated in ambient D₂ at 500 °C. Nonpolarized light. Lower curve: Voigt profile fit consisting of five curves of equal line width.

a ⁸²Se-H bond and agrees with the theoretical suggestion of the involvement of hydrogen in the defect giving rise to the μ modes.⁷ A suitable model for the 1992- and 2001-cm⁻¹ features is two inequivalent Se-H bonds aligned parallel (SeH_{||}) and “perpendicular” (SeH_⊥) to the *c* axis, respectively.

The alignment of SeH_{||} and SeH_⊥ implies that the two modes can be considered independently in order to fit the experimentally observed frequencies gathered in Tables I and II. The eigenvalues of the vibrational Hamiltonian with the Morse potential are^{16,17}

$$\omega = \omega_e - 2x\omega_e. \quad (2)$$

Here, ω_e is the harmonic frequency and x is the anharmonicity parameter. Both ω_e and x are inversely proportional to $\sqrt{\mu}$, where μ is the reduced mass of the Se-H bond,

$$1/\mu = 1/m_{\text{H/D}} + 1/\chi M_{\text{Se}}. \quad (3)$$

The parameter χ accounts for the coupling to the lattice.¹⁸ The best-fit frequencies obtained from Eqs. (2) and (3) are listed in Tables I and II. As one can see, the agreement between calculated and experimental values is fairly good.

The theory assigns the 1992- and 2001-cm⁻¹ modes to the cadmium vacancy decorated with two hydrogen atoms, V_{Cd}H₂.^{7,8} This model is fully supported by our study. A

TABLE II. Experimental (Exp.) and best-fit frequencies (in cm⁻¹) obtained with Eqs. (2) and (3) for SeH_⊥. Fitting parameters ω_e , x , and χ refer to ⁷⁸Se and H isotopes.

	⁸² Se	⁸⁰ Se	⁷⁸ Se	⁷⁷ Se	⁷⁶ Se
	SeH _⊥				
Exp.	2001.0	2001.3	2001.7	2001.8	2002.0
Fit	2001.1	2001.4	2001.7	2001.8	2002.0
	SeD _⊥				
Exp.	1460.3	1460.8	1461.2	1461.5	1461.7
Fit	1460.4	1460.8	1461.2	1461.5	1461.7
$\omega_e = 2175.8$	$x = 0.0400$		$\chi = 0.9521$		

similar defect ($V_{\text{Zn}}\text{H}_2$) was also investigated in ZnO.^{14,15} There, hydrogen forms two inequivalent O–H bonds, with one bond aligned parallel to the c axis (3312 cm^{-1}), whereas the second one forms an angle of $100 \pm 5^\circ$ with c (3350 cm^{-1}). If ZnO is treated in the mixture of H_2 and D_2 , the $V_{\text{Zn}}\text{HD}$ complex is formed with the LVMs shifted by $2\text{--}3\text{ cm}^{-1}$ from those of the “pure” $V_{\text{Zn}}\text{H}_2$ and $V_{\text{Zn}}\text{D}_2$ complexes. Contrary to ZnO, no additional modes were observed in a CdSe sample, which could be related to the $V_{\text{Cd}}\text{HD}$ complex, after the treatment with both hydrogen isotopes.

LVMs of $V_{\text{Cd}}\text{HD}$ in CdSe were not considered theoretically. However, we suppose that the coupling between hydrogen atoms is weaker in $V_{\text{Cd}}\text{H}_2$ than in $V_{\text{Zn}}\text{H}_2$. Our suggestion is based on the comparison of the Se–H (1.46 \AA) and O–H (0.97 \AA) bond lengths and the mean distances Cd–Se (2.63 \AA) and Zn–O (1.97 \AA) of regular CdSe and ZnO lattices.¹⁹ Simple geometric consideration reveals that the H–H distance in $V_{\text{Cd}}\text{H}_2$ is about 17% larger than that in $V_{\text{Zn}}\text{H}_2$. In our opinion, the relatively large distance between the two hydrogen atoms comprising $V_{\text{Cd}}\text{H}_2$ accounts for the “missing” modes of the $V_{\text{Cd}}\text{HD}$ complex.

$V_{\text{Zn}}\text{H}_2$ in ZnO can also exist in a metastable state where both O–H bonds are aligned “perpendicular” to the c axis of the lattice.¹⁵ The energy difference between the metastable and the ground states is $75 \pm 9\text{ meV}$, with the activation barrier of the hydrogen motion within the vacancy of $0.96 \pm 0.12\text{ eV}$. In the case of $V_{\text{Cd}}\text{H}_2$, theory predicts the energy difference between the two orientations of the Se–H bonds to be equal to 3 meV ,⁷ which means that the metastable state of the defect should be easy to detect. We could not, however, detect additional lines in the spectra, which might be interpreted as LVMs of a metastable state of $V_{\text{Cd}}\text{H}_2$. A possible explanation for this result is a weak coupling between the Se–H bonds

within the Cd vacancy, which should result in only a marginal difference in the LVM frequencies of the “perpendicular” Se–H bonds in the metastable versus the ground state. Theoretical studies are called for to verify this suggestion.

Finally, we note that Chen *et al.* detected the 1992- and 2001- cm^{-1} lines in CdSe samples which were not intentionally doped with hydrogen. We observed a similar behavior in our as-received material. Weak 1992- and 2001- cm^{-1} lines showed up after annealing of the samples in argon atmosphere at 400°C . This leads us to the conclusion that hydrogen is a common impurity in CdSe and may even occur in an IR inactive form. A similar situation takes place in ZnO,²⁰ where the “hidden” species is an interstitial molecule, H_2 .²¹ More work is needed to understand the properties of hydrogen in CdSe.

IV. SUMMARY

CdSe single crystals thermally treated in H_2 and/or D_2 gas at 500°C were investigated by IR absorption spectroscopy. Two features, at 1992 and 2001 cm^{-1} , appear in the hydrogenated sample as a result of the treatment. Isotope substitution experiments identify these LVMs as stretch vibrational modes of two Se–H bonds aligned parallel and “perpendicular” to the c axis of the crystal. The underlying defect is assigned to the Cd vacancy passivated by two hydrogen atoms, ($V_{\text{Cd}}\text{H}_2$). The $V_{\text{Cd}}\text{H}_2$ complex is shown to be stable up to 500°C .

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