Reassignment of the O_{Te}-V_{Cd} complex in CdTe

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An IR absorption study of single-crystal CdTe annealed in $CdSO_4$ vapor at 850 °C is presented. It is shown that such a treatment results in the appearance of two absorption lines ν_1 and ν_2 at 1096.8 and 1108.4 cm^{-1}, respectively [G. Chen *et al.*, Phys. Rev. Lett. **96**, 035508 (2006); Phys. Rev. B **75**, 125204 (2007)]. Each of these features is accompanied by weaker lines. The intensities of each set of lines match the natural abundance of the sulfur isotopes. The ν_1 and ν_2 modes are assigned to the stretch vibrations of a sulfur-oxygen complex, SO_2^*. The number of oxygen atoms involved in SO_2^* was deduced from the relative intensity of an IR absorption line related to the ^{18}O isotope.

I. INTRODUCTION

CdTe is presently the material for pixel x-ray, γ-ray, α-particle, and β-particle detectors,[1,2] and solar panels.[3–5] For a large number of applications, carrier lifetime is a key parameter determining the quality of a semiconductor device. Impurities and defects have a strong impact on the carrier lifetime; that is why the understanding of their properties is necessary to manufacture devices with highest efficiencies. Vibrational mode spectroscopy is a tool that provides a wealth of information about impurities with masses less than those of the host atoms. Both constituents of CdTe are located in the bottom part of the periodic table, which opens up the possibility to study a significantly larger number of impurities and defects compared to most technologically important semiconductors. For example, local vibrational modes (LVMs) of substitutional magnesium, calcium, and sulfur in CdTe were already reported.[6,7]

Recently, Chen *et al.* performed a Fourier-transformed infrared (FTIR) absorption study of CdTe grown by the vertical Bridgman technique.[8,9] The samples were synthesized from pure CdTe and appropriate amounts of TeO_2 or CdO. A number of IR absorption lines was observed and assigned to different oxygen-related complexes. In particular, a signal at 349.8 cm^{-1} was interpreted as a local vibrational mode of substitutional oxygen at the Te site, O_{Te}. This assignment was confirmed theoretically by Zhang *et al.*, who found that O_{Te} results in a LVM at 341 cm^{-1}.[10]

Chen *et al.* also detected two IR absorption lines at 1096.8 (ν_1) and 1108.4 cm^{-1} (ν_2), which were assigned to O_{Te} perturbed by the nearby Cd vacancy, O_{Te}-V_{Cd}. Another pair of lines at 2198.7 (ν_4) and 2210.5 cm^{-1} (ν_5) was associated with the first overtones of the ν_1 and ν_2 fundamentals.

In our opinion, the assignment of the ν_1 and ν_2 lines to LVMs of O_{Te}-V_{Cd} meets serious difficulties. The vibrational mode of O_{Te} was found to have a frequency of 349.8 cm^{-1}. The assignment of the 1096.8- and 1108.4-cm^{-1} modes to O_{Te}-V_{Cd} implies an effective bond stiffness approximately nine times higher than in O_{Te}. Such a strengthening of the O-Cd bond can be hardly visualized if a Cd vacancy becomes trapped at O_{Te}.

Here we present the results of an FTIR absorption investigation of single-crystal CdTe doped from the $CdSO_4$ vapor, which unambiguously show that the 1096.8- and 1108.4-cm^{-1} lines are due to the stretch modes of a sulfur-dioxygen (SO_2^*) complex rather than O_{Te}-V_{Cd}.

II. EXPERIMENTAL

For this study we employed CdTe single crystals doped with chlorine, which were grown via the traveling heater method. The samples were sealed in quartz ampules filled with 16-mg $CdSO_4$ powder and 250-mbar argon gas. The treatments were performed at 850 °C for 315 min.

IR absorption spectra were recorded with a Bomem DA3.01 Fourier spectrometer equipped with a KBr beam splitter, a globar light source, and a liquid-nitrogen-cooled mercury-cadmium-telluride detector. The spectral resolution was 0.2−0.5 cm^{-1}. The measurements were performed in a He exchange-gas cryostat equipped with ZnSe windows.

III. RESULTS AND DISCUSSION

Figure 1 shows a section of an IR absorption spectrum obtained at 8 K from a CdTe sample treated in $CdSO_4$ at 850 °C. Two lines at 1096.8 (ν_1) and 1108.4 cm^{-1} (ν_2) previously reported by Chen *et al.* dominate the spectrum.[9] We emphasize that all features labeled in the figure were observed only as a result of the treatment.

In addition to the ν_1 and ν_2 modes, a number of weaker lines located at 1082.8, 1089.5, 1094.3, and 1101.1 cm^{-1} are also seen in the figure. Note that the lines at 1094.3 and 1101.1 cm^{-1} can be also spotted in Fig. 1 of Ref. 9. Unfortunately, the spectra published by Chen *et al.* were presented in the range 1092 to 1112 cm^{-1}, which does not allow us to verify if the other lines were also observed by these authors.

The relative intensities of the 1108.4- (ν_2), 1101.1-, and 1094.3-cm^{-1} lines (92.9 : 1.5 : 5.6), as well as those located at 1096.8, 1089.5, and 1082.8 cm^{-1} (94.6 : 0.9 : 4.5), are independent of the sample history and are very close to the natural abundances of the sulfur isotopes ^{32}S (95%), ^{33}S (0.75%), and ^{34}S (4.2%), respectively, which leads us to the
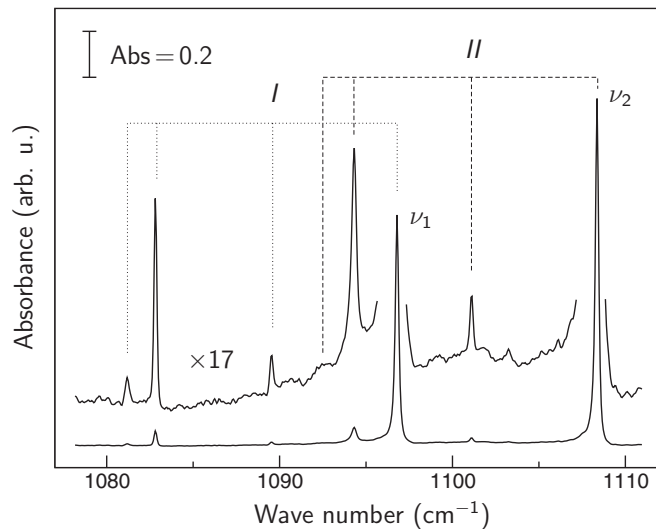
FIG. 1. Section of IR absorption spectra obtained at 8 K from a CdTe sample treated in CdSO$_4$ at 850 °C. Unpolarized light.

conclusion that the defect(s) giving rise to the IR absorption lines presented in Fig. 1 involve(s) sulfur.

Based on this, we propose that the lines seen in the figure can be divided into two groups, labeled I and II, each of which originates from the stretch modes of an SO$_n^*$ complex (see Table I). The asterisk is employed to distinguish the defect from a free SO$_n$ molecule. The involvement of oxygen into the defect was convincingly demonstrated by Chen *et al.* and is supported by our sample treatment. Note that the vibrational mode of SO in the gas phase is 1138 cm^{-1},[11] i.e., close to the frequencies observed in our experiments.

A number n of oxygen atoms comprising SO$_n^*$ can be obtained from the intensity of the vibrational modes related to the ^{18}O isotope whose natural abundance is 0.2%. The strongest of the ^{18}O-related modes corresponding to the ^{32}S^{16}O$_{n-1}$^{18}O* species should occur in the spectra with the intensity close to $n \times 0.2\%$ of the dominant line due to ^{32}S^{16}O$_n^*$.

Careful inspection of the spectrum presented in Fig. 1 reveals a weak line at 1081.2 cm^{-1}, which matches the expected position of the ^{18}O-related mode from group I. Its relative intensity with respect to the rest of the modes suggests that there are two oxygen atoms in the defect complex, SO$_2^*$.

In contrast, no clear signal due to the ^{18}O-related mode from group II could be found in the spectra, whose expected position is also labeled in Fig. 1. A possible explanation comes from the asymmetry of the IR absorption lines, implying a Fano resonance[12,13] between the LVMs and the continuum of the electronic states in the conduction and/or valence band

TABLE I. Local vibrational modes (in cm^{-1}) of SO$_2^*$. See also text.

		^{32}S^{16}O$_2^*$	^{33}S^{16}O$_2^*$	^{34}S^{16}O$_2^*$	^{32}S^{16}O^{18}O*
Group I	Exp.	1096.8	1089.5	1082.8	1081.2
	Calc.	1096.8	1089.5	1082.7	1081.2
Group II	Exp.	1108.3	1101.1	1094.3	–
	Calc.	1108.3	1101.1	1094.3	1092.5

of CdTe. As follows from the spectra, the neighboring to the expected position of the ^{18}O-related mode line, located at 1094.3 cm^{-1}, is broader than the rest of the signals. We suggest, therefore, that the Fano resonance also broadens the ^{18}O-related mode from group II so that it cannot be detected. This suggestion, however, needs to be verified in the ^{18}O-enriched CdTe samples.

The presence of two oxygen atoms bound to a single sulfur atom in the SO$_2^*$ complex implies that the defect should reveal symmetric and asymmetric stretch LVMs. In the case of the free molecule, the asymmetric and symmetric stretch modes have frequencies of 1362 and 1151 cm^{-1}, respectively.[11,14–16] Since SO$_2$ is not a linear molecule, the "symmetric" transition is not forbidden in dipole approximation and can be detected in IR absorption. The corresponding intensity, however, is about one order of magnitude less than that of the asymmetric mode.[17,18] We found no unambiguous spectroscopic evidence for the existence of the symmetric LVM due to SO$_2^*$, which is presumably related to the weakness of the corresponding signals.

In support of our assignment, the harmonic frequencies of the asymmetric stretch mode of SO$_2^*$ in the valence force approximation[19] were estimated neglecting the influence of the bend mode. The stretch modes were obtained from the secular equation

$$\|\boldsymbol{GF} - \omega^2 \boldsymbol{I}\| = 0, \qquad (1)$$

where $\boldsymbol{I}$ is the identity matrix and

$$\boldsymbol{G} = \begin{pmatrix} \mu_1^{-1} & m_S^{-1}\cos\varphi \\ m_S^{-1}\cos\varphi & \mu_2^{-1} \end{pmatrix}, \quad \boldsymbol{F} = \begin{pmatrix} k & 0 \\ 0 & k \end{pmatrix}. \qquad (2)$$

Here, $\mu_{1(2)}^{-1} = m_S^{-1} + m_{O_1(O_2)}^{-1}$ are the reduced masses of the two oxygen atoms bound to the sulfur atom and φ is the ∢ OSO angle. The "best-fit" values, which are listed in Table I, are obtained for $k = (6.6 \pm 0.1) \times 10^2$ N/m and $\varphi = 120 \pm 2°$. As one can see, the agreement between calculated and experimental values is very good. For comparison, the ∢ OSO angle and force constant of free SO$_2$ are equal to 119.5° and 10.77×10^2 N/m, respectively.[20]

In addition to the ν_1 and ν_2 modes, Chen *et al.* also reported IR absorption lines at 2198.7 (ν_4) and 2210.5 cm^{-1} (ν_5), which were interpreted as first overtones of the 1096.8- and 1108.4-cm^{-1} fundamentals.[9] In dipole approximation, optical transitions for a harmonic oscillator with $\Delta n = \pm 2$ are forbidden. Here n is the principal quantum number of the oscillator. Anharmonicity renders these transitions allowed. The standard approximation for the vibrational frequency and the transition probability for overtones of real oscillators is the Morse potential.[21] The quasiexact eigenvalues $E_n = \hbar\omega(n)$ of the vibrational Hamiltonian with the Morse potential are

$$\omega(n) = \omega_0(n + 1/2) - \omega_0 x_e(n + 1/2)^2, \qquad (3)$$

where x_e is the anharmonicity parameter and ω_0 is the harmonic frequency. It follows from Eq. (3) that fundamental
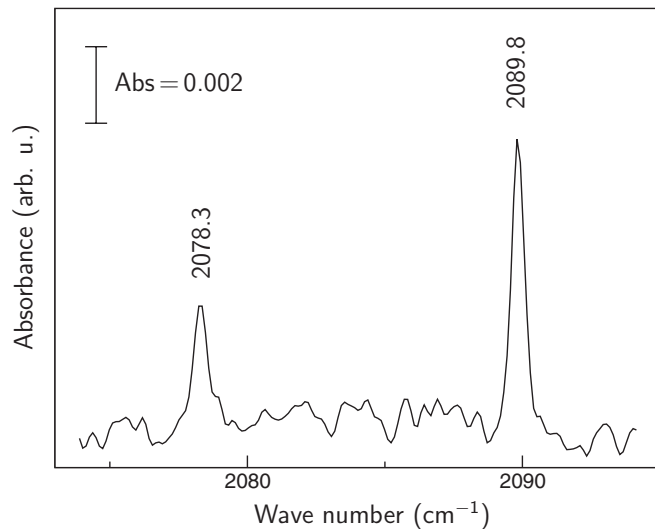
FIG. 2. Section of IR absorption spectra obtained at 8 K from a CdTe sample treated in $CdSO_4$ at 850 °C. Unpolarized light.

and first overtone frequencies of the anharmonic oscillator are $\omega_1 = \omega(1) - \omega(0) = \omega_0 - 2\omega_0 x_e$ and $\omega_2 = \omega(2) - \omega(0) = 2\omega_0 - 6\omega_0 x_e$, respectively. Moreover,

$$2\omega_1 \geqslant \omega_2. \qquad (4)$$

This inequality, however, is not fulfilled in the case of the ν_1 mode, since

$$2\nu_1(2 \times 1096.8 = 2193.6 \,\text{cm}^{-1}) < \nu_4(2198.7 \,\text{cm}^{-1}),$$

and casts doubts on the assignment of ν_4 as an overtone of ν_1.

The Morse potential has proven to be a fairly good approximation that successfully describes properties of numerous molecules and chemical bonds. Keeping this in mind, we looked up our spectra of CdTe doped with SO_2^* for other LVMs which could comply with Eq. (4). Two IR absorption lines at 2078.3 and 2089.8 cm^{-1} were found which satisfy the needed requirements (see Fig. 2). From Eq. (3) the anharmonicity parameters x_e of the ν_1 and ν_2 modes were found to be close to each other and equal to 0.048 and 0.051, respectively.

In order to find out if the SO_2^* defect has a level in the band gap of CdTe, we also performed IR absorption measurements under band-gap illumination with a Hg lamp. No influence on the intensities of the IR absorption lines presented in Fig. 1 was found, which indicates that the defect is electrically inactive.

Chen *et al.* established that the ν_1 and ν_2 modes are not independent: As the temperature rises, the frequency difference between the two lines decreases until they merge around 300 K.[9] We have detected identical behaviors for other pairs of lines from groups I and II for the temperatures up to 45 K, which agrees with their assignment as due to the different sulfur isotopes of SO_2^*. At $T > 45$ K the IR lines experience significant broadening so that only the dominant ν_1 and ν_2 modes can be investigated. Similar to the fundamentals, the frequency difference between the 2078.3- and 2089.8-cm^{-1} lines decreases as the temperature rises, which complies with the expected behavior of the ν_1 and ν_2 overtones.

To explain the merging of the ν_1 and ν_2 modes, Chen *et al.* proposed a model of "dynamic switching of the O_{Te}-V_{Cd} dangling bond among the four $\langle 111 \rangle$ directions" for the defect axis at increasing temperature.[9] In view of our findings, however, it is clear that this model has to be reconsidered.

An important question concerns the position of SO_2^* in the CdTe lattice. The simplest traps to consider are Cd and Te vacancies and/or tetrahedral interstitial sites T_{Cd} and T_{Te}. Different orientations of SO_2 trapped at these sites with respect to the crystallographic axes of CdTe should result in different local vibrational modes. We speculate that an energetic barrier separates metastable states of the molecule which gives rise to the ν_1 and ν_2 modes. At elevated temperatures, however, the rotational barrier is overcome and only one line occurs in the IR absorption spectrum.

The means to verify this model and to get further insight into the microscopic properties of SO_2^* are experiments on uniaxial stress splitting of the LVMs. This technique reveals directly the symmetry of point defects embedded into cubic crystals.[22] Moreover, stress-induced dicroism of the IR absorption lines can, in turn, shed light on the energetic barrier between different orientations of the molecule in the lattice.[23,24] Separate theoretical studies are also called for to reveal the structure of SO_2^*.

Finally, we note that Chen *et al.* reported 1094.1- (γ_1), 1107.5- (γ_2), and 1126.6-cm^{-1} (γ_3) absorption lines in CdSe, which were also assigned to local vibrational modes of substitutional oxygen at the Se site perturbed by the nearby Cd vacancy.[25] Taking into account the similarity between the γ modes in CdSe and the ν modes of SO_2^* in CdTe, we have inspected the spectra presented by Chen *et al.* for the presence of signals which might be related to the sulfur isotopes.

Indeed, weak lines at 1093.5, 1099.7, and 1112.5 cm^{-1} can be spotted in Fig. 3 of Ref. 25. Polarization properties of the first two are identical to the γ_2 mode, whereas the 1112.5-cm^{-1} line seems to be correlated with γ_3. Based on the frequencies and intensities of these signals, we tentatively assign them to the sulfur isotopes. In particular, the LVMs at 1093.5 and 1099.7 cm^{-1} match the ^{34}S-^{16}O and ^{33}S-^{16}O replicas of the γ_2 mode (1107.5 cm^{-1}), respectively, whereas the 1112.5-cm^{-1} line seems to be the ^{34}S-^{16}O replica of γ_3 (1126.3 cm^{-1}). Taking the analogy between CdTe and CdSe even further, we speculated that the γ modes in CdSe also originate from the SO_2^* species. The presence of three instead of two lines is explained by the lowering of the crystal symmetry from the zinc blende (CdTe) to wurtzite (CdSe).

In order to corroborate our suggestion, preliminary IR absorption experiments on CdSe treated with $CdSO_4$ were performed. As expected, the same γ modes previously reported by Chen *et al.* were detected in our samples, which strongly suggests that these also originate from SO_2^*.

IV. SUMMARY

CdTe samples treated with $CdSO_4$ at 850 °C were investigated by means of Fourier-transformed IR absorption spectroscopy. Seven IR absorption lines were observed in the range 1080 to 1110 cm^{-1} and assigned to the fundamental asymmetric stretch vibrational modes of a sulfur-dioxide complex SO_2^*.

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