

## Urbach tail, disorder, and localized modes in ternary semiconductors

Ismardo Bonalde, Ernesto Medina, and Miguel Rodríguez

*Centro de Física, Instituto Venezolano de Investigaciones Científicas, Apartado 21874, Caracas 1020-A, Venezuela*

S. M. Wasim, G. Marín, and C. Rincón

*Centro de Estudios de Semiconductores, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela*

A. Rincón and C. Torres

*Grupo de Polímeros, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela*

(Received 14 August 2003; revised manuscript received 9 December 2003; published 11 May 2004)

We analyze the role of localized modes, produced by structural disorder, in the formation of the optical-absorption edge in semiconductors. Such modes give rise to an additional energy  $h\delta\nu_d$ , above the average of the optical modes in the ordered sample. In the present study, this interpretation is confirmed experimentally from a study of infrared absorption spectra of several samples of the semiconductor CuGaTe<sub>2</sub>. The high value of  $h\nu_p$  found in these samples, higher than the average of the 14 Raman modes of the ordered sample, is in good agreement with the average of all the optical and localized modes. Previous models involving disorder are discussed and derived from the thermal/disorder broadening of a harmonic oscillator with average frequency associated with the measured phonon modes. Our quantitative interpretation in terms of phonon frequency shift can be extended to a more general class of crystalline/amorphous semiconducting materials.

DOI: 10.1103/PhysRevB.69.195201

PACS number(s): 78.20.Ci, 78.30.Ly, 71.35.Cc

### I. INTRODUCTION

The thermal broadening of the band tails that modify the optical-absorption edge according to Urbach-Martienssen rule is a very general phenomenon for insulators such as ionic and organic crystals and semiconductors. The absorbed intensity  $\alpha(E)$  of the incident photons of energy  $E$  follows the relation

$$\alpha(E) = \alpha_0 \exp[-\sigma(E_0 - E)/k_B T], \quad (1)$$

where  $\sigma$  is known as the steepness parameter.  $\alpha_0$ ,  $\sigma$ , and  $E_0$  are independent of the incident photon energy. Such temperature dependence reveals the involvement of exciton-phonon interactions.<sup>1</sup> The steepness parameter  $\sigma$  of the Urbach rule, describing the optical-absorption coefficient just below the band edge in insulators and semiconductors, is given by the empirical relation<sup>1</sup>

$$\sigma = \sigma_0 \frac{2k_B T}{h\nu_p} \tanh\left(\frac{h\nu_p}{2k_B T}\right). \quad (2)$$

Here  $\sigma_0$  is a temperature-independent constant proposed to be inversely proportional to the exciton-phonon interaction strength. The energy parameter  $h\nu_p$  was considered initially to be the energy of phonons involved in the formation of photon absorption edge, and the Urbach energy  $E_U = k_B T/\sigma$  was expected to be a direct measure of the temperature-induced disorder. Later, the Urbach tail was also associated to the topological or site disorder contribution. Cody *et al.*<sup>2</sup> proposed a phenomenological model that accounts for the latter contribution to the Urbach energy by including a temperature-independent term proportional to the deformation  $X$  produced by disorder

$$E_U(T) = \frac{k_B \Theta}{\sigma_0} \left[ \frac{1+X}{2} + \frac{1}{\exp(\Theta/T) - 1} \right], \quad (3)$$

where  $\Theta$  is the Einstein characteristic temperature that corresponds to the mean frequency of phonon excitations of a system of noninteracting harmonic oscillators. Although this model satisfactorily explained the  $E_U$  versus  $T$  data of a variety of materials,<sup>3</sup> it deviates significantly from the observed behavior of the Urbach energy in ternary compounds.<sup>4</sup> This is to be expected because the model of Cody *et al.* considers only the effect of topological disorder and, therefore, may not be applicable to crystalline semiconductors that have structural defects caused by substitutional disorders, cation and anion vacancies, and interstitials.

To explain the  $E_U$  versus  $T$  data of different ternary compounds, Wasim *et al.*<sup>4</sup> introduced a modified version of Eq. (3),

$$E_U(T) = \frac{k_B \Theta}{\sigma_0} \left[ \frac{1+P}{2} + \frac{N}{\exp(\Theta/T) - 1} \right], \quad (4)$$

where the empirical parameters  $P$  and  $N$  were quantitatively correlated with disorder characterization of the samples in terms of deviation from molecularity and valence stoichiometry. Very good agreement with the experimental data was reported.

Defects not only affect the temperature dependence of the Urbach tail, but also seem to modify the energy  $h\nu_p$  involved in its formation. In the case of Cu-III-VI<sub>2</sub> ternary compound semiconductors<sup>4,5</sup> and their chalcopyrite-related Cu-III<sub>3</sub>-VI<sub>5</sub> and Cu-III<sub>5</sub>-VI<sub>8</sub> ordered defect phases,<sup>6</sup> the value of  $h\nu_p$  was found to be much larger than the highest optical mode of these semiconductors. In Ref. 4, it was proposed *qualitatively* that this additional phonon energy in  $h\nu_p$  and the variation of  $E_U$  with  $T$  could come from localized modes

originating from a large concentration of cation-cation, cation-anion, and other intrinsic disorders present in these materials.

In this paper we propose a theoretical model which can account for the Urbach tails in terms of only the average phonon energy  $h\nu_p$  as a function of disorder. This contrasts with the usual identification of a single phonon mode coupled to the Urbach tail. It is shown that Eqs. (3) and (4) can be understood by introducing the new localized phonon frequency within the expression of the quantum-mechanical lattice deformation potential. To test quantitatively if the proposed model accounts for the existence of contributions to the Urbach energy from localized modes, created by substitutional disorder, and that the extra phonon energy in  $h\nu_p$  comes from such modes, we measured the infrared optical absorption in three single-crystal samples of  $\text{CuGaTe}_2$  of known stoichiometry.

The energy of the peaks observed in the infrared optical-absorption spectra of each sample, that could not be associated with donor or acceptor level transitions or discarded as replicas of phonons at higher energies, is averaged with those of the 14 Raman modes to estimate the magnitude of  $h\nu_p$ . We compared the phonon energy obtained from three different analyses, that is, (i)  $h\nu_p$  from a fit to Eq. (2) of the experimental absorption data, (ii)  $h\nu_p^*$  estimated from a combined analysis of the infrared and Raman modes, and (iii)  $h\nu_p$  from our proposed theory of the Urbach tail in terms of shifts in the average phonon frequency due to disorder. This comparison provides strong quantitative evidence that high values of phonon energies involved in the formation of the Urbach tail are associated with structural defects caused by the deviation from ideal stoichiometry and also confirms the validity of the present theoretical model.

## II. THEORY ON THE URBACH ENERGY AND LOCALIZED MODES

The empirical models expressed in Eqs. (3) and (4) for the Urbach energy can be derived from a single formulation in terms of the potential fluctuations  $D$  due to lattice vibrations of frequency  $\nu_p$ . As derived by Sumi and Toyozawa<sup>7</sup>

$$D^2 = 2Sk_B T_{Urbach} = N_{opt} \frac{1}{2} |V|^2 \coth\left(\frac{h\nu_p}{2k_B T}\right), \quad (5)$$

where  $V$  is the exciton-phonon coupling,  $S = (1/2)N_{opt}|V|^2/h\nu_p$  is the energy gain of the exciton due to the interaction with the lattice vibrations, and  $N_{opt}$  is the number of optical modes. We assume in this relation that all modes involved are optical modes of average frequency  $\nu_p$ . From this expression one can obtain

$$k_B T_{Urbach} / \sigma_0 = E_U = \frac{h\nu_p}{2\sigma_0} \coth\left(\frac{h\nu_p}{2k_B T}\right), \quad (6)$$

where it is needed to divide by  $\sigma_0$ , a sample-dependent dimensionless parameter, to be in accordance with the empirical formula of Eq. (2). We suggest that both the thermal and structural contributions are encoded<sup>8</sup> in the values of  $h\nu_p$  through either the regular modes of the defect free sample or

the localized modes produced by disorder. In order to demonstrate this, we show below that the structural parameter  $X$  of Cody *et al.* or  $P$  of Wasim *et al.*<sup>4</sup> is related to the shifted average phonon frequencies as disorder increases. One can use the definition of the hyperbolic cotangent in terms of exponentials, and rewrite the expression in Eq. (6) as

$$E_U = \frac{h\nu_p}{\sigma_0} \left( \frac{1}{2} + \frac{1}{\exp(h\nu_p/k_B T) - 1} \right). \quad (7)$$

Now  $\nu_p$  can be split into  $\nu_p^0 + \delta\nu_d$ , where  $\nu_p^0$  represents the phonon energy of the structurally ordered defect free phase and  $\delta\nu_d$  describes the deviations in the involved phonon energies due to disorder

$$E_U = \frac{h\nu_p^0}{\sigma_0} \left( \frac{1 + \delta\nu_d/\nu_p^0}{2} + \frac{1 + \delta\nu_d/\nu_p^0}{\exp(h\nu_p/k_B T) - 1} \right). \quad (8)$$

From this expression one can identify the temperature-independent parameter  $X$  or  $P$  as  $\delta\nu_d/\nu_p^0$ . Note that  $\delta\nu_d/\nu_p^0$  is not assumed to be small and is not treated as an expansion parameter. Such identification agrees quantitatively with the curve of  $P$  versus  $h\nu_p$  in Fig. 8 of Ref. 4, where the slope is  $1/h\nu_p^0$  within experimental errors. This slope is an important physical feature of the theory, because it identifies the mode average of the pure system independent of the disorder. However, care must be taken when the factor  $\delta\nu_d/\nu_p^0$  is related physically to the parameter  $X$  of Cody *et al.* in amorphous materials. This is because, in this case, a univocal reference to an ordered structure is not possible. Nevertheless, one can still define a dominant phonon frequency  $h\nu_p$  for the amorphous state, and use Eq. (6) to describe the photon absorption in such a state. By doing so, we obtain a very good fit to the data of amorphous Si reported by Cody *et al.* in Fig. 2 in their paper, with  $h\nu_p = 60$  meV. It remains to be determined whether this high value of phonon frequency is actually observed from infrared studies.

It can be noted that the parameter  $\delta\nu_d$  appears in both the numerator and the denominator of the second term in Eq. (8). An attempt to relate  $N$  in Eq. (4) to the parameters of Eq. (8) yields a complicated function of temperature and shifted phonon frequency  $\delta\nu_p$ , function from which it is difficult to extract any useful physical information.

## III. EXPERIMENTAL METHODS

The details of the growth and structural characterization of the single crystals of  $\text{CuGaTe}_2$  already appear in Ref. 9. Samples obtained from the ingots grown by standard vertical Bridgman method are termed CGTVB, and those by tellurization of Te at 650 and 700 °C are labeled as CGT650 and CGT700, respectively. The infrared absorption spectra of each sample after averaging over 400 scans were recorded at  $T = 300$  K in the energy range from 50 to 350 meV by a Perkin Elmer model System 2000 FTIR spectrophotometer. In order to eliminate the effect of air, its spectrum was also registered and then subtracted from the sample spectra.

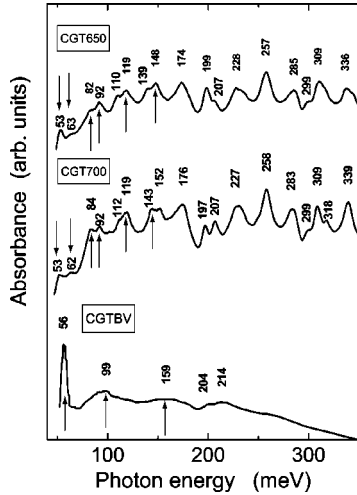


FIG. 1. Infrared absorption spectra at room temperature between 50 and 350 meV of CuGaTe<sub>2</sub> samples: CGT650, CGT700, and CGTVB. The arrows indicate the peaks associated with localized modes.

#### IV. RESULTS AND DISCUSSION

From the Raman spectra observed<sup>9</sup> at 80 K, the number of lattice vibrational modes in CuGaTe<sub>2</sub> should be 14. The infrared absorption spectra between 50 and 350 meV of CuGaTe<sub>2</sub> samples are shown in Fig. 1, and the energies of the peaks are given in Table I. The energy of the Raman modes varies from the lowest at 7 to the highest at 28 meV. The simple average of the 14 Raman modes, which is around 18 meV in this compound, is smaller than the phonon energy  $h\nu_p$  associated with the Urbach tail, which varies from 29 to 46 meV. We note that the weighted average using the peak intensities of the Raman spectra  $\sum I_i \nu_i / \sum I_i$  differs from the simple average by about 1%. We remark that the simple average, which has worked well in our studied system, may not work in other systems.

Considering an error of about 2 meV in determining the energy of the infrared peaks, these can be classified uniquely into three groups: (i) those that appear at the same energy in some of the samples, (ii) those that are not common to any sample, and (iii) others above 150 meV that can be represented as the sum of the peaks at lower values. Some of the peaks that are observed at the same energy in some of the samples and others that are only present in a particular sample, in general, would most likely correspond either to the transitions from donor or acceptor defect levels to the conduction or valence bands. They could also be attributed to the additional high-energy phonon modes originating from the intrinsic defects present in these samples. Examining these possibilities, we found that the absorption peaks at 111 and 181 meV in CGT600 and 111 meV in CGT650 agree well with the activation energy of possible acceptor levels at 110 and 180 meV, which are calculated<sup>11</sup> for this compound from the effective-mass approximation. For this reason, these peaks should not correspond to the high-energy phonon modes that originate from the cation and anion disorders.

The peaks observed at energies above 150 meV are not considered to be high-energy localized phonon modes. This

TABLE I. Energy (meV) of the vibrational modes observed by infrared spectra between 50 and 350 meV of CGT650, CGT700, and CGTVB samples of CuGaTe<sub>2</sub>. The energy of the highest optical mode of the ordered chalcopyrite compound is 28 meV. The numbers in parenthesis in the columns indicate the energy of the phonon replicas or the activation energy  $E_A$  of the acceptor levels. The phonon energies with asterisk are the localized modes above the ordered chalcopyrite optical band. These energies, when simple averaged with the Raman modes given in Ref. 10, are used to calculate the energy  $h\nu_p^*$  given in Table II.

Peak number	CGT650	CGT700	CGTVB
1	53*	53*	56*
2	63*	62*	
3	82*	84*	
4	92*	92*	99*
5	110( $E_A$ )	112( $E_A$ )	
6	119*	119*	
7	139(1,3)	143(1,4)	
8	148*	152(2,4)	159*
9	174(1,6)	176(1,6)	
10	199(1,8)	197(1,7)	
11	207(2,7)	207(2,7)	204
12	228(1,9)	227(1,9)	217(1,8)
13	257(3,9)	258(3,9)	
14	285(3,10)	283(3,10)	
15	299(4,11)	299(4,11)	
16	309(1,13)/(3,12)	309(1,13)/(3,12)	
17		318(4,11)	
18	336(1,14)	339(1,14)	

is because they are found to be the sum of two phonon modes of lower energies which are already taken into account in the calculation of the average phonon energy  $h\nu_p$ . Hence discarding these peaks, the contribution to the phonon energy  $h\nu_p$  involved in the Urbach tail, in addition to Raman modes, is expected to be only from those modes marked with an asterisk in Table I.

The average of the 14 Raman modes of CuGaTe<sub>2</sub> reported in Ref. 10 and those vibrational modes with asterisk in Table I is given as  $h\nu_p^*$  in Table II for each sample. In the same table the values of  $h\nu_p$  and  $\sigma_0$  derived from the optical-absorption data<sup>10</sup> are given. A reasonably good agreement is achieved. The slightly lower values of  $h\nu_p$  in comparison with  $h\nu_p^*$  could be explained in terms of the possible existence of localized modes between 30 and 50 meV, which are

TABLE II. Phonon energies  $h\nu_p$  and  $\sigma_0$  associated with the Urbach tail as measured from optical-absorption measurements. The energies  $h\nu_p^*$  are obtained by simple averaging all the Raman and localized modes of each sample studied.

Sample	$\sigma_0$	$h\nu_p$ (meV)	$h\nu_p^*$ (meV)	$\delta\nu_d/\nu_p^0$
CGT650	0.53	36.2	40.5	1.01
CGT700	0.95	29.0	34.9	0.61
CGTVB	0.61	40.5	42.8	1.25

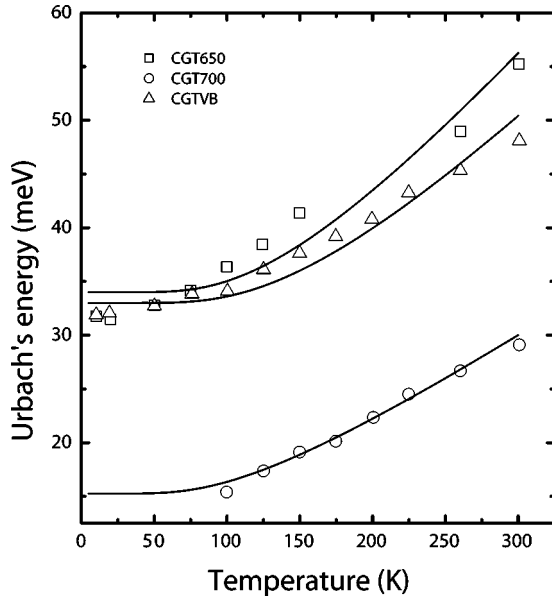


FIG. 2. The Urbach energy as a function of temperature for CuGaTe<sub>2</sub> samples CGT650, CGT700, and CGTVB. The solid lines correspond to numerical evaluations of Eq. (6).

not taken into account in the calculation of  $h\nu_p^*$ . On the other hand, in CuGaTe<sub>2</sub>  $h\nu_p^0 = 18$  meV, and the values of  $\delta\nu_d/\nu_p^0$  for each studied sample are shown in Table II. As expected, these values are similar to the values of  $P$  calculated for other Cu ternary compounds in Ref. 4. The similarity of the values of  $h\nu_p$  and  $h\nu_p^*$  would imply, according to the model proposed above, that the data of the Urbach energy versus temperature, obtained directly from the slope of the experimental optical-absorption versus photon energy graphs,<sup>10</sup> should follow Eq. (6) with the values of  $h\nu_p$  and

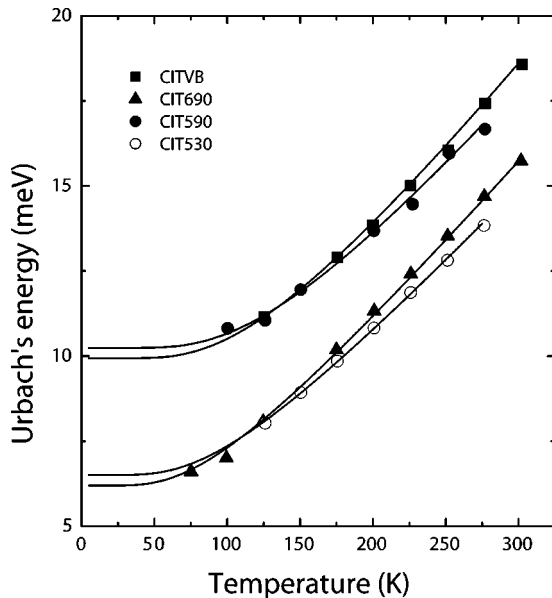


FIG. 3. The Urbach energy data from Ref. 4 as a function of temperature for CuInTe<sub>2</sub>. The solid lines correspond to numerical evaluations of Eq. (6).

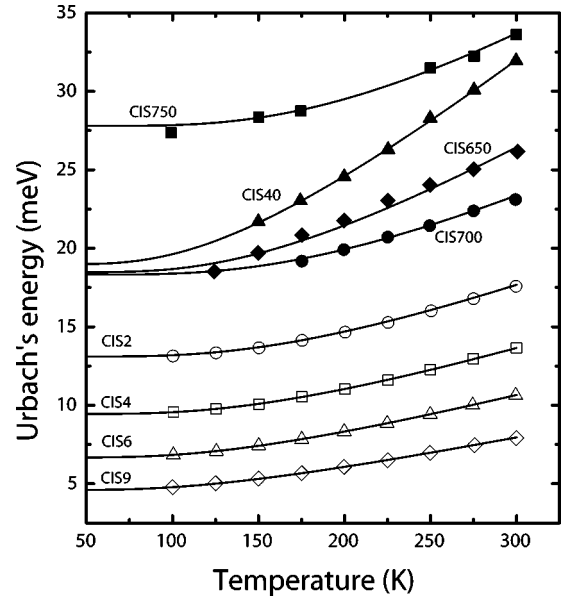


FIG. 4. The Urbach energy data from Ref. 4 as a function of temperature for CuInSe<sub>2</sub>. The solid lines correspond to numerical evaluations of Eq. (6).

$\sigma_0$  reported in Table II. The comparisons for the CuGaTe<sub>2</sub> samples are shown in Fig. 2, where a good agreement is observed in the whole range of measured temperatures. A much better agreement is found for the reanalyzed data of CuInTe<sub>2</sub> and CuInSe<sub>2</sub> of Ref. 4, as can be seen from Figs. 3 and 4, respectively. For the latter comparisons we have used the values of  $h\nu_p$  and  $\sigma_0$  given in Table II of Ref. 4. Such good matches confirm the interpretation made earlier<sup>4</sup> in the case of CuInSe<sub>2</sub> and CuInTe<sub>2</sub> that in the formation of the Urbach tail both the Raman modes and additional modes originating from lattice defects caused by cations, anion vacancies, interstitials, and antisites disorders are involved. The observed phonon energy  $h\nu_p$ , as obtained from the Urbach tail, represents the average of these modes. We emphasize that the agreement of the Urbach energy data with the theory presented here is better than that previously secured with the two physically motivated, fitting parameters of Ref. 4 (see Figs. 5 and 6 in this reference).

We note that the quality of the comparisons depends on the value of  $h\nu_p$ . This value will determine if the system is in the low- (quantum) or high- (classical) temperature regimes, and will be crucial in establishing the location of the crossover from temperature-independent to temperature-dependent behavior implied by the quantum oscillator model. This crossover is determined by the expression  $T_{cross} = h\nu_p/2k_B$ . Here the crossover temperature depends on the disorder, because  $\nu_p$  is a function of the disorder parameter  $\delta\nu_d$ . In the previous models  $T_{cross}$  was fixed at a chosen Einstein temperature. This causes these models to have a linear temperature dependence in a region where the data display clearly an upward curvature (see Fig. 5 in Ref. 4).

## V. CONCLUSIONS

To summarize, our interpretation of the Urbach energy as a function of disorder has yielded a general model with only



one adjustable parameter  $\sigma_0$ . Such model should be applicable to the analysis of disorder and the Urbach tail in other crystalline/amorphous materials. In fact, this model has been verified<sup>12</sup> further for the so-called ordered vacancy compounds  $\text{CuIn}_3\text{T}_5$  and  $\text{CuIn}_5\text{T}_8$  whose structural character is very different from the compound studied here, but also generate defects that are describable by Eq. (8). The model should also apply to binary compounds, although defect energies are much higher and, thus, variations in the average phonon frequencies should be small. It is noteworthy that binary compounds such as  $\text{CdTe}$ ,  $\text{ZnSe}$ , and  $\text{ZnTe}$ , whose Urbach tails have been analyzed in the literature,<sup>1</sup> show a value of  $h\nu_p$  much higher than the highest energy values associated with longitudinal- or transverse-optical modes. We believe that this is a manifestation of localized modes, and not a high-symmetry effect as suggested in previous analysis.<sup>1</sup>

The variations in the average optical phonon energy

coupled to excitons  $h\nu_p$ , producing the band tails, have been verified quantitatively as a function of disorder from stoichiometry correlations and direct experimental infrared measurements. The remaining parameter  $\sigma_0$  has traditionally been associated with the exciton-phonon coupling strength. In the present interpretation such coupling drops out, because of an equal weight given *a priori* to all optical and localized phonon modes. Nevertheless this is very likely only a good approximation, and going beyond such a premise should yield an exciton-phonon coupling-dependent theory (see Ref. 7).

#### ACKNOWLEDGMENTS

This work was supported by grants from CONICIT (Contracts Nos. G-97000670 and NM-08) and CDCHT-ULA (Contracts No. C-917 and C-918).

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