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Urbach tail of gadolinium trihydride films

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Abstract The fundamental absorption edge of the gadolinium trihydride has been studied by performing optical transmission measurements at temperatures ranging from 298 K to 353 K. Urbach tails and the photon absorption spectra give information about the exciton dynamics, distinguishing between free and trapped excitons in the lattice. Our experimental results can be accounted for in terms of the theory of Toyozawa and co-workers, which ascribe the Urbach tail to the momentary localization of excitons due to phonon interaction.

Introduction

In a large variety of insulating and semiconducting materials the spectral dependence of the absorption coefficient alpha at low-energy tail of the fundamental optical absorption edge can be expressed by the empirical relation, which is called Urbach rule [1, 2],

$$\alpha(E) = \alpha_o \exp\left[\sigma(T)\frac{E - E_o}{KT}\right] \tag{1}$$

where $\alpha(E)$ is the absorption coefficient, E is the photon energy, α_o and E_o are the characteristic parameters of the material, $\sigma(T)$ the steepness parameter, and T the temperature.

This implies that a plot of $\ln(\alpha)$ against E near the band edge can be represented by a straight line. The extrapolating of these lines corresponding to different temperatures tends to converge at a point defined by α_o and E_o in Eq. 1. The parameter E_o, also called the converging energy, is necessarily higher than the optical band gap energy [3]. The relation $KT/\sigma(T)$, which is the width of the exponential tail, is called the Urbach energy E_U. This dependence has been confirmed experimentally as a kind of universal law and has stimulated many efforts for its theoretical explanation. In order to explain the origin of the Urbach tail, a number of theoretical studies have been carried out. Among them, two types of theories seem to be worth mentioning at present.

One of them, developed by Dow and Redfield [4], ascribes the Urbach tail to the ionization of excitons by internal electric microfield produced by phonons, charged impurities, lattice disorder, etc. The tunnelling of the electron away from the hole through the Coulomb barrier leads to an exponentially decaying density of states below the absorption threshold, resulting in Urbach rule. In this model, the influence of the phonon field on the relative motion of the electron–hole pair and therefore exciton interband scattering is the dominant mechanism. This model applies well to III–V and II–VI compounds where the exciton–phonon coupling is relatively weak and the excitons are mostly free [5].

The other one, developed by Toyozaka and co-workers [6–8], ascribes the Urbach tail to the influence of phonon fields on the center-of-mass motion of excitons, where exciton interband scattering is important. Urbach rule follows from an interplay between the mobile nature of the exciton and the

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tendency of the vibrating lattice to localize the exciton momentarily, i.e momentary self-trapping of excitons [9]. This model applies more to highly ionic crystals such as alkali halides and oxides, where the exciton–phonon coupling is large.

The steepness parameter $\sigma(T)$ in Eq. 1 has been found to follow the relation

$$\sigma(T) = \sigma_o \frac{2KT}{h\nu_p} \tanh\left(\frac{h\nu_p}{2KT}\right) \tag{2}$$

where σ_o is a constant independent of temperature, and $h\ \nu_p$ corresponds to the energy of phonons associated with the Urbach tails. Equation 2 corresponds theoretically to the thermal average over potential fluctuations of a harmonic lattice in the dispersionless approximation with linear exciton–phonon interactions [10]. Within such theory, the steepness constant σ_o is inversely proportional to the exciton–phonon-coupling constant g:

$$\sigma_o = \frac{s}{g} \tag{3}$$

where s is the steepness index. This index has been determined by Schreiber and Toyozawa [8] to be 1.5 ± 0.06 for direct absorption edges and 0.8 ± 0.05 for indirect ones. Therefore, the exciton–phonon-coupling constant can be deduced from the experimental values of σ_o. The self-trapping of excitons occurs when g is larger than a critical value

$$g_c = 1 - (2\nu)^{(-1)} \tag{4}$$

where ν is the number of nearest-neighboring sites for exciton intersite transfer.

On the other hand, E_U is expected to be a direct measure of the temperature-induced disorder and reflects the thermal occupancy of phonon states in the crystal [7, 11]. From the standard treatment of Urbach tails in crystalline semiconductors, it is then concluded that $K\ T/\sigma$ is proportional to the thermal average $\langle U^2\rangle_T$. This thermal average, like the Debye–Waller factor, is a measure of the square of the displacement U of the atoms from their equilibrium position.

Gadolinium hydrides have many characteristic properties in common with the hydrides of heavy rare-earth metals. The dihydride has metallic properties which gradually disappear as the hydrogen content approach the trihydride composition and the metal film transforms into a transparent phase. As this metal-insulator (MI) transition is reversible at room temperature and moderate gas pressures, several technical applications are conceivable, such as use as a switchable mirror. In the present work, we report a systematic study of the optical absorption edge in GdH_3 film at different temperature.

Experimental methods

The samples are prepared as follows. First, 100 and 300 nm, polycrystalline gadolinium films were deposited under UHV conditions at room temperature on glass by rf-sputtering system. The base pressure was in the order of 1×10^{-8} mbar. The film thickness was measured with a quartz microbalance. Subsequently, a 15 nm Pd layer was deposited to protect the gadolinium films from oxidation and to promote H_2 dissociation. The Pd film was grown at room temperature to prevent alloy formation with the gadolinium. Then the sample was transferred into a gas loading cell with optical windows and electrical leads. The sample was hydrogenated to the trihydride phase, and this process was controlled by resistance measurements. The purity of H_2 was 99.999%. The transmission spectra (300–3,000 nm) of both GdH_3 films were recorded with Hitachi UV/Vis/NIR Spectrophotometer. To eliminate the effect of the substrate and the Pd layer on the determination of the absorption spectra of the GdH_3 film, we determined $T(\lambda) = I_{300}/I_{100}$, where I_{300} and I_{100} denote the intensities transmitted through the 300 nm GdH_3 and 100 nm GdH_3 film , respectively, and λ is the wavelength of the photons. The optical absorption coefficient α at different temperature between 293 K and 353 K was obtained with the following relation:

$$\alpha(\lambda) = -\frac{\ln(T(\lambda))}{d_{eff}} \tag{5}$$

where $d_{eff} = 231\,\text{nm}$ is the difference of film thickness of the two films, taking also into account the lattice expansion of 15.9% between metal gadolinium and GdH_3 [12].

Experimental results and discussion

The logarithmic variation of α with photon energy E, just below the fundamental absorption edge at several temperatures between 293 K and 353 K, is shown in Fig. 1 for GdH_3 film. To maintain the clarity of the figure, a $\ln(\alpha)$ versus E plot is given for limited number of temperatures.

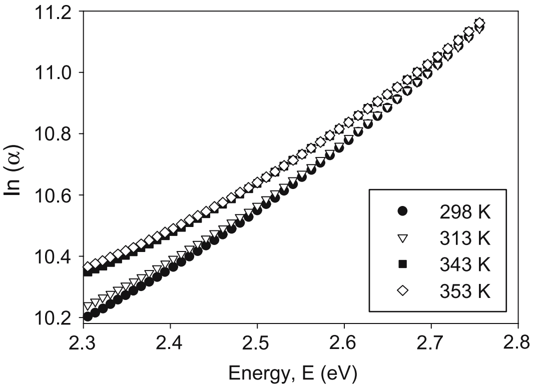

Fig. 1 Logarithmic variation of the absorption coefficient α with the photon energy E at several temperatures between 298 K and 353 K, just below the fundamental absorption edge, for a GdH_3 film

A linear dependence is observed within a certain energy range up to one order of magnitude in α at each temperature. In agreement with Urbach rule, the extrapolation of the fitted continuous lines in the this range of α converges to a single point. The corresponding values of α_o and E_o at the converging point for the GdH_3 sample studies in this work are: $E_o = 2.75$ eV and $\alpha_o = 6.7 \times 10^4\,\mathrm{cm}^{-1}$.

The other Urbach tail parameters of GdH_3 film have been deduced from the experimental spectra according to Eqs. 1 and 2 as follows: $\sigma(T)$ is calculated from the slope of the fitted Urbach tail represented by Eq. 1. These values are plotted in Fig. 2 as a function of temperature. To get an estimate of the phonon energy associated with the Urbach tail, in general, the data in Fig. 2 should be fitted to Eq. 2 with σ_o and $h\nu_p$ as adjustable parameters. But, because of strange curve structure in Fig. 2. One may argue that the calculation of σ_o and $h\nu_p$ through this way is not correct.

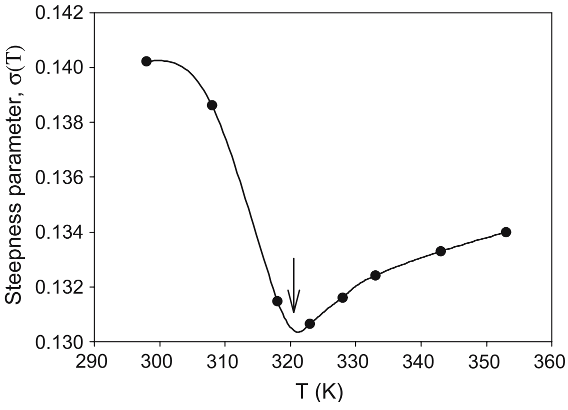

Fig. 2 The steepness parameter σ as a function of temperature for GdH_3 film. Only the data points for, ($T > 320$ K), could be fitted very well to Eq. 2

According to Fig. 2, at low temperature, (<320 K), it is difficult to fit the data to Eq.(2) because it is behaves differently from the Eq. 2, but at high temperature (>320 K), the calculated value of σ approaching a constant value. Therefore, developing $\tanh(h\nu_p/2KT)$ in a power series and taking the first two terms, Eq. 2 becomes:

$$\sigma(T) = \sigma_o\left[1 - \frac{1}{3}\left(\frac{h\nu_p}{2KT}\right)^2\right] \tag{6}$$

So, from a graph between $\sigma(T)$ and $1/T^2$, (*figures not included*), the values of σ_o and $h\nu_p$ at high temperature can be obtained. These values are: $\sigma_o = 0.1602$, $h\ \nu_p = 28.7$ meV.

Exciton–phonon-coupling constant can be deduced from the experimental steepness parameters using Eq. 3. We find $g = s/\sigma_o = (0.85 \pm 0.05)/0.1602 = 5.3 \pm 0.3$ for the indirect edge in GdH_3. This value exceed the critical limit required for self-trapping of excitons, whatever the value of ν, see Eq. 4. This value indicates that the self-trapped state is stabilized for the excitons in this range of temperature.

Figure 3 shows isoabsorption curve at 3.28×10^{-4} cm^{-1} and the variation of $E_U = KT/\sigma(T)$ against T of GdH_3, is shown in Fig. 4.

To compare the experimental Urbach energy with a theoretical model, Cody et al. [11] proposed an empirical relation that takes into account both the interaction of electrons and excitons with phonons and the static structural disorder. This empirical relation takes the form:

$$E_U(T,X) = \frac{K\Theta}{\sigma_o}\left(\frac{1+X}{2} + \frac{1}{\exp(\Theta/T) - 1}\right) \tag{7}$$

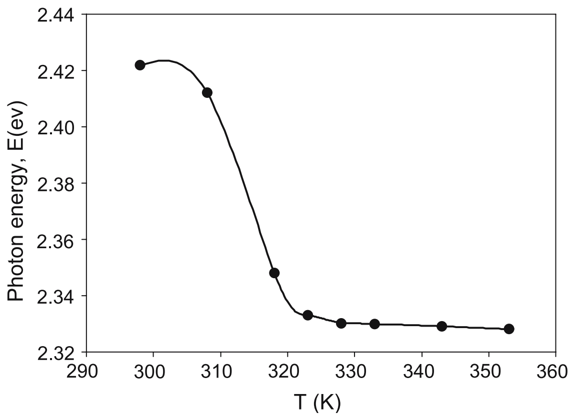

Fig. 3 Isoabsorption curve of GdH_3 at $\alpha = 3.28 \times 10^4\,cm^{-1}$

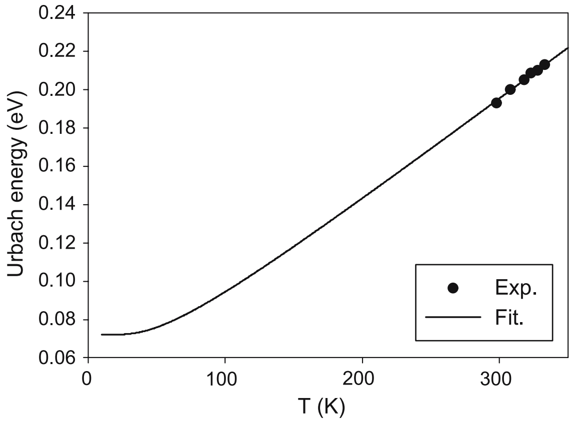

Fig. 4 The Urbach energy E_U as a function of temperature for GdH_3 film (circles). The solid curve represents a fit to Eq. 7 with the parameter $X = 0.725 \pm 0.0728$

where Θ is the Einstein temperature, relaed to the Debye temperature by $\Theta \sim 3/4\ \Theta_D$, and X is the temperature-independent structural disorder parameter.

The best fit, shown by solid line in Fig. 4, is obtained with $\Theta = 166.5\ K$, and the value of $X = 0.725 \pm 0.0728$.

Conclusion

We have shown that the GdH_3 film displays essentially mixed behaviors at the fundamental absorption edge. In addition we would like to point out the possibility to use the exciton absorption or emission spectra as a probe of ferromagnetic phase transition, in comparison to, ferroelectric phase transition [13]. Also, the high phonon energy $h\nu_p$ has its origin in structural disorder, i.e. there is some source of order-disorder-type of phase transition in GdH_3 film. At high temperature (>320 K), the internal field-induced polarization of exciton is smeared out because of randomization. And the spectral dependence of the absorption edge follows the Urbach rule. According to the exciton–phonon interaction model of Toyozawa and co-workers, the exciton–phonon-coupling constant in GdH_3 can be evaluated from the slope of the Urbach tail. These coupling constant largely surpasses the critical value, predicting that excitons are self-trapped in GdH_3 at high temperature. In contrast, at low temperature (<320 K), it is expected that a net polarization appears, implying that the inversion symmetry of the exciton is broken.

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