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The Urbach tail of absorption and photoluminescence spectra in EuSe

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Abstract. The steepness constant in the Urbach rule for the absorption spectra of EuSe has been determined—for the first time—to be 0.79. The magnitude implies that the strength of the electron–phonon interaction relating to the $4f^7 \rightarrow 4f^65d(t_{2g})$ exciton transition is as strong as that in alkali halides, and that the exciton is described by a scheme of strong electron–phonon coupling. Furthermore, it has been found that the higher-energy tail of the photoluminescence band increases exponentially with decreasing photon energy by over an order of magnitude, which shows that the photoluminescence band is related to the Urbach rule in the absorption spectra. Also, it has been confirmed, from the consistency of the Urbach tail for the photoluminescence and the absorption, that the photoluminescence in EuSe is the reverse of the $4f^7 \rightarrow 4f^65d(t_{2g})$ exciton transition and hence that the photoluminescence band is intrinsic.

1. Introduction

It is well known that non-metallic materials have a clear rise of the absorption coefficient—what is called the absorption edge. At a finite temperature, absorption occurs even below the absorption edge energy, because the incident photon is absorbed with the assistance of the elementary excitation which occurs at finite temperature. Therefore, the optical absorption spectrum shows the tail below the absorption edge at a finite temperature. The tail part near the absorption edge in various non-metallic materials can be expressed empirically as follows:

$$\alpha(E, T) = \alpha_0 \exp \left[-\frac{\sigma(T)(E_0 - E)}{k_B T} \right] \quad (1)$$

where the absorption coefficient α is a function of the photon energy E and the temperature T . E_0 is the photon energy where the spectrum at each temperature converges, α_0 is the absorption coefficient at $E = E_0$, and $\sigma(T)$ is called the steepness coefficient and depends on the temperature. According to equation (1), $\sigma(T)/k_B T$ expresses the degree of steepness near the absorption edge.

Urbach [1] first discovered that equation (1) was applicable in silver halides, in 1953, so equation (1) is called the Urbach rule. After that, the Urbach rule was found to be applicable in general to various non-metallic materials, even organic molecular solids, ferroelectric materials and amorphous materials. As the elementary excitation required for the appearance of the Urbach tail in the absorption spectrum, a phonon is an easy choice, and the value of σ depends on the temperature as follows [2]:

$$\sigma = \sigma_0 \left(\frac{2k_B T}{\hbar\omega} \right) \tanh \left(\frac{\hbar\omega}{2k_B T} \right) \quad (2)$$

where σ_0 is called the steepness constant, is independent of temperature and takes an inherent value for each material. $\hbar\omega$ is the average energy of phonons which contribute to the Urbach tail in absorption spectra.

Each material has its own value of the steepness constant. The absorption edge of each material is ascribed to the excitonic transition, so the steepness constant reflects the nature of the excitonic state which is influenced by the phonon field. In particular, the nature of the relaxed photo-excited state, that is, either a free-exciton state or a self-trapped-exciton state, can be classified according to the magnitude of the steepness constant for various materials [3]. Table 4.1. in [3] shows the correlations between the observed steepness constant σ_0 and the nature of relaxed exciton, whether it is a free or a self-trapped state. If the free state is stable, the sharp emission lines are observed just below the absorption edge, while if the self-trapped state is stable, the Stokes-shifted broad emission band is observed.

The Urbach tail is usually observed in the absorption spectrum. However, the photoluminescence spectrum is expected to contain information about the Urbach tail in the absorption spectrum, if the emission process is just the inverse of the absorption process and the two energy levels (a ground state and an excited state), which have to do with the optical transition, are in the thermal equilibrium state [4]. According to the principle of detailed balance, the following Einstein relation holds between the emission $L(E, T)$ and the absorption $\alpha(E, T)$ [4]:

$$L(E, T) \propto \exp\left(-\frac{E}{k_B T}\right) \alpha(E, T). \quad (3)$$

Therefore,

$$L(E, T) \propto \exp\left[\frac{(\sigma - 1)E}{k_B T}\right] \quad (4)$$

where the emission intensity decreases toward lower photon energy if σ is larger than unity, while the emission intensity increases toward lower photon energy if σ is less than unity. This suggests that whether the emission spectrum shows the Stokes-shifted emission band whose intensity on the higher-energy side of the peak obeys equation (4) or shows the emission lines with a sharp zero-phonon line whose intensity on the lower-energy side of the peak obeys equation (4) [4] should depend on the steepness coefficient σ . It was firstly confirmed that the lower-energy tail of the free-exciton emission spectra of PbI_2 and HgI_2 obey the Urbach rules [5, 6], which has been attributed to the existence of the metastable self-trapped exciton state. There has been no report that a stable self-trapped-exciton emission obeys the Urbach rule, as far as we know.

Europium chalcogenides have been known as typical magnetic semiconductors, where the interaction between the localized 4f spin and the conduction electron or the photo-excited electron plays an important role in the optical and the electrical properties. However, there has been relatively little interest shown as regards the electron-phonon interaction. Although the exponential dependence of the absorption coefficient on the photon energy was investigated for EuO [7], EuSe [8], and EuTe [9], the steepness constant was not derived. Therefore, we have investigated the electron-phonon interaction associated with the lowest optical transition—that is, the $4f^7 \rightarrow 4f^6 5d(t_{2g})$ exciton transition—and have obtained the value of the steepness constant from the absorption spectrum in EuSe . Although EuS , EuSe , and EuTe show the Stokes-shifted photoluminescence band below the energy edge and its tentative assignment is thought to be the $4f^6 5d(t_{2g}) \rightarrow 4f^7$ transition [10], the assignment has not been clear up to now. In this report, we have examined whether the emission spectrum in EuSe obeys the Urbach rule or not and have examined the nature of the photoluminescence band in EuSe .

2. Experimental details

Single crystals of EuSe were grown by the chemical vapour transport method. To measure the absorption and photoluminescence spectra, we used a 20 cm monochromator (Jobin–Yvon HR-20IR). As a detector of light, a Si PIN photo-diode and a cooled photomultiplier (RCA 7102) were used for the absorption and photoluminescence measurements, respectively. The 488 nm line of an Ar-ion laser was used for the excitation of the photoluminescence. The photoluminescence spectra measured were calibrated with a standard halogen lamp and the photoluminescence intensity is expressed in proportion to the photon number per unit photon energy. The absorption and photoluminescence spectra were measured for the same sample to avoid the effect of sample dependence.

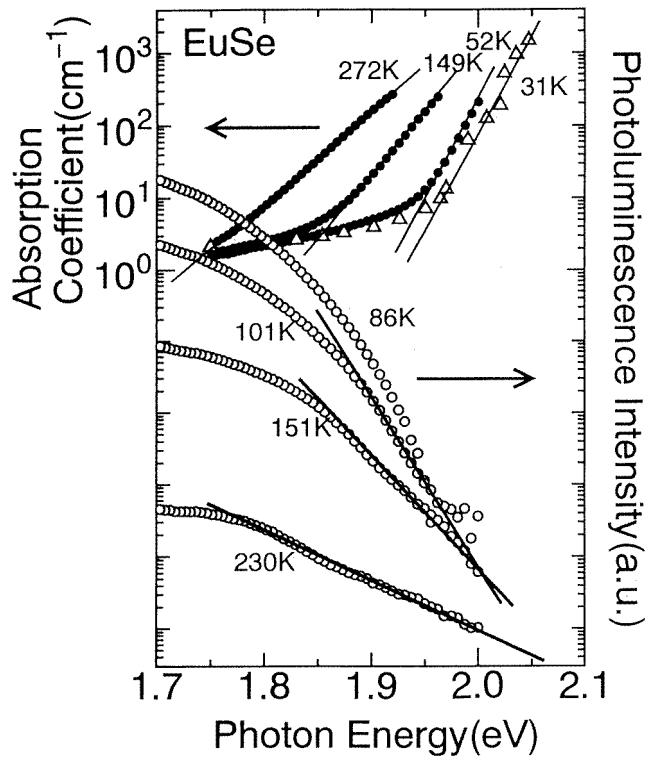


Figure 1. Semilogarithmic plots of the absorption (closed circles) and the photoluminescence spectra (open circles) in EuSe at several temperatures. The absorption spectrum at 31 K (triangles) shows the experimental results of Batlogg and Wachter [8]. The solid lines show the results obtained by fitting with equations (1) and (4) for the absorption and the photoluminescence spectra, respectively.

3. Results and discussion

Figure 1 shows the temperature dependence of the absorption (open circles) and photoluminescence spectra (closed circles) for EuSe with the thickness of $50 \mu\text{m}$ in the semilogarithmic plots. The absorption spectrum at 31 K (triangles) shows the experimental results of Batlogg and Wachter [8]. As seen from the absorption spectra near the absorption

edge in figure 1, the absorption coefficient at each temperature increases exponentially toward higher photon energy. In particular, at 272 K, the exponential increase in the absorption coefficient ranges over more than two orders in magnitude. Furthermore, the steepness of each spectrum becomes larger as the temperature is lowered to around 52 K, and this behaviour is consistent with equation (1). As seen from the absorption spectrum at 31 K—and this temperature satisfies the condition $k_B T \ll \hbar\omega$ as found later—the exponential increase in the absorption coefficient ranges over more than two orders of magnitude. This supports the assertion that the Urbach tail observed at high temperatures is due to the $4f^7 \rightarrow 4f^6 5d(t_{2g})$ transition and not due to higher transitions. The lower-energy parts in the absorption spectra at 31 K, 52 K and 149 K have residual absorptions and deviate from the Urbach rule. This residual absorption does not depend on temperature, so it may be associated with crystal imperfections.

The entire lineshape of the photoluminescence spectra for EuSe is almost Gaussian and is well described within the strong-electron–phonon-coupling scheme [11]. On the other hand, as seen from the photoluminescence tail on the higher-energy side in figure 1, the photoluminescence intensity increases exponentially toward lower photon energy. Furthermore, the spectral steepness around the tail becomes larger as the temperature is decreased. Note that the exponential increase in photoluminescence intensity is observed in the *same* energy region as that in which the absorption coefficient obeys the Urbach rule. However, below around 100 K—for example, as in the photoluminescence spectra obtained at 86 K shown in figure 1—we cannot observe the photoluminescence obeying the Urbach rule in the photon energy region in which the absorption coefficient obeys the Urbach rule.

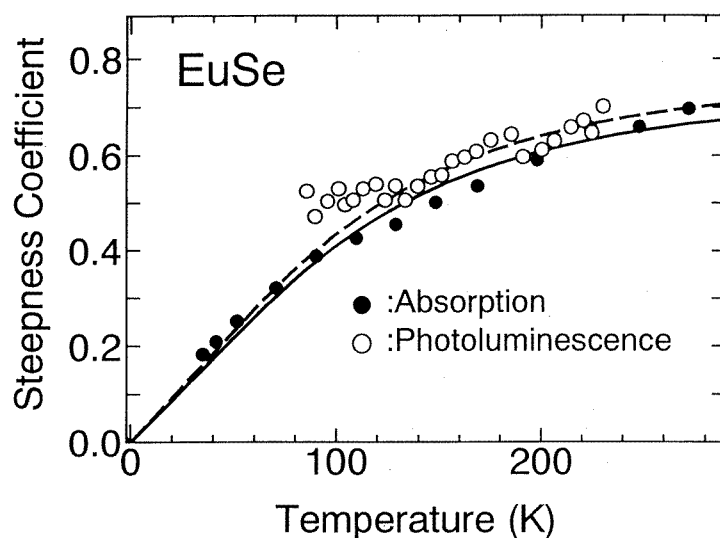


Figure 2. A comparison of the steepness coefficient for EuSe obtained from the analysis of the absorption spectra (closed circles) with that from the analysis of the photoluminescence spectra (open circles). The solid and the broken curves show the results obtained by fitting with equation (2) for the absorption and the photoluminescence, respectively.

Figure 2 shows two sets of the steepness coefficients for EuSe as functions of the temperature, which were obtained from the absorption and photoluminescence spectra shown in figure 1. The experimental values of the steepness coefficient are plotted as

the closed and open circles for the absorption and the photoluminescence, respectively. The photoluminescence spectrum was fitted using equation (4) in the tail part where the absorption coefficient obeys the Urbach rule, and the steepness coefficient was derived. The steepness coefficients for the photoluminescence are not plotted below around 100 K, since, below this temperature, we cannot find the Urbach tail in the photoluminescence spectra in the same energy region as that in which the absorption spectra obey the Urbach rule.

The solid and the broken curves in figure 2 show the results from a fitting using equation (2) for the absorption and the photoluminescence, respectively. The two fittings were done for the present experimental values of the steepness coefficient above 30 K and 120 K for the absorption and the photoluminescence, respectively, in order to obtain as accurate a value of σ_0 as possible for the later discussion. The steepness constants σ_0 and the photon energies $\hbar\omega$ which are obtained for the absorption and the photoluminescence are listed in table 1. Both of the phonon energies $\hbar\omega$ are comparable with the maximum phonon energy, 22.7 meV of LO(Γ), of EuSe measured by an earlier Raman scattering study [12, 13]. The value of $\hbar\omega$ is reasonable, since it has been found through the analysis of the photoluminescence for EuS and EuSe [11] that the relaxed $4f^65d$ exciton couples strongly with the LO phonon.

Since the two values of the steepness coefficient agree above around 120 K, it is found that the two levels related to the absorption and emission—that is, the ground state and the excited state—are in thermal equilibrium with each other, and that the energetic distribution between them obeys the Boltzmann distribution law $\exp(-E/k_B T)$. Therefore, this result suggests strongly that the nature of the photoluminescence band observed near the band edge must be intrinsic.

Table 1. The steepness constant σ_0 and the phonon energy $\hbar\omega$ in the Urbach rule determined from the absorption and the photoluminescence measurements.

Method	Steepness constant σ_0	Phonon energy $\hbar\omega$ (meV)
Absorption	0.79	29.1
Photoluminescence	0.75	29.6

As mentioned above, the higher-energy tail of the photoluminescence band in EuSe deviates from the Urbach rule below around 100 K, although the absorption coefficient in EuSe obeys the Urbach rule. Since the rough spectral lineshape of the photoluminescence band can be described using the configuration coordinate model of strong electron–phonon coupling [11], the lineshape is expected to be Gaussian at the low temperatures at which the population of excitons concentrates at the bottom of the adiabatic potential in the relaxed excited state. Therefore the Urbach tail in photoluminescence is expected to disappear, which is consistent with the experimental results.

The present experimental result for the steepness constant for EuSe is about 0.8, as shown in table 1. The fundamental absorption edge for EuSe arises from the allowed $4f^7 \rightarrow 4f^65d(t_{2g})$ exciton transition, so, according to Toyozawa [3], the self-trapped state is expected to be more stable than the free state as the relaxed excited state, which agrees with the experimental result that EuSe exhibits a photoluminescence band with the Stokes-shifted Gaussian shape. Furthermore, it is found that the magnitudes of the steepness constants in EuSe are comparable with those of materials which have strong electron–phonon interactions, such as the alkali halides NaCl, KBr, and KI whose steepness constants are 0.76, 0.79, and 0.82 [3].

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References

- [1] Urbach F 1953 *Phys. Rev.* **92** 1324
- [2] Mahr H 1962 *Phys. Rev.* **125** 1510
- [3] Toyozawa Y 1986 *Excitonic Processes in Solids* (Berlin: Springer) ch 4, p 201
- [4] Sumi H and Toyozawa Y 1971 *J. Phys. Soc. Japan* **31** 342
- [5] Goto T, Takeda J and Matsuoka M 1988 *J. Lumin.* **40–41** 481
- [6] Goto T, Takeda J, Ishihara T and Matsuoka M 1987 *J. Lumin.* **38** 55
- [7] Wachter P 1964 *Helv. Phys. Acta* **37** 637
- [8] Batlogg B and Wachter P 1977 *Solid State Commun.* **24** 569
- [9] Schmutz L E, Dresselhaus G and Dresselhaus M S 1978 *Solid State Commun.* **28** 597
- [10] Streit P 1973 *Phys. Kondens. Mater.* **15** 284
- [11] Akimoto R, Kobayashi M and Suzuki T 1994 *J. Phys. Soc. Japan* **63** 4616
- [12] Silberstein R P, Schmutz L E, Tekippe V E, Dresselhaus M S and Aggarwal R L 1976 *Solid State Commun.* **18** 1173
- [13] Hatano T, Akimoto R, Kobayashi M, Suzuki T and Endo S 1995 *J. Phys. Chem. Solids* **3–4** 531