Radiative recombination in crystalline As$_2$S$_3$

K. Murayama and M. A. Bösch

Bell Laboratories, Holmdel, New Jersey 07733

(Received 7 April 1981)

Two photoluminescence bands characterized by their excitation energy are observed in orpiment (c-As$_2$S$_3$). We assign the emission band with the peak energy of 1.53 eV to defect-related bound-exciton recombination. The luminescence band at 1.25 eV is induced by band-to-band excitation and may be understood by the self-trapping of an exciton.

Photoluminescence spectra from crystalline arsenic chalcogenides have been reported within the last ten years without providing a unanimous picture of the radiative recombination mechanism in these materials. Since the As-chalcogenides are also model substances for studying disorder, we have chosen c-As$_2$S$_3$ (orpiment) to investigate the steady-state luminescence properties in more detail. We should mention that universal results are difficult to achieve for orpiment, which is only available as a natural mineral.

Absorption, photoluminescence, and excitation spectra should reveal clearly the prevailing radiative-recombination mechanisms. Kolomiets et al.[1] reported a luminescence band with a peak energy of 1.26 eV and a half-width of 0.41 eV at 77 K. Mollot et al.[2] found a similar spectrum slightly (0.1 eV) shifted to lower energy at 1.6 K. In contrast to these findings, Street et al.[3] and Bösch et al.[4] reported a main luminescence band at 1.6 eV. These differences are not due to crystal quality, but rather are due to the appearance of two different luminescence processes, as will be outlined in this paper.

High-quality natural crystals of yellow orpiment (Siberia) were cleaved into sheets prior to measurements of the luminescence and optical absorption. An Ar-ion laser provided the excitation light for the luminescence, which was analyzed by a double monochromator and detected with a GaAs photomultiplier or Si-PIN photodiode. Photon counting was accomplished with computer on-line data acquisition and calibration.

The absorption spectra observed with polarized light are shown in Fig. 1. A flat absorption region at low photon energy and a steep rise of the absorption at higher photon energies are general features,[5] the latter indicating the onset of band-to-band transitions. Superimposed on the regular absorption tail we observe a shoulder at 2.5 eV. Zakis and Fritzsche[6] reported an absorption band at the same position. They proposed an impurity-absorption process, namely, the high-energy transition between a shallow impurity level and the band edge.

The luminescence spectra obtained from the same sample with different excitation photon energies are

revealed in Fig. 2. The excitation energy of 2.54 eV is close to the peak position of the above-discussed shoulder in the absorptance. The peak energy for this high-energy luminescence is 1.53 eV for intensity units of photons/cm^2 eV (or 1.59 eV in the case of W/cm^2 eV). The half-width obtained by fitting the high-energy side of the spectrum to a Gaussian line shape is 0.36 eV. The second luminescence band in Fig. 2 is excited by 2.71-eV radiation positioned into the absorption edge. Similar line shapes but much larger Stokes shifts are apparent.

Figure 3 reveals the photoluminescence excitation spectra. The excitation curves for luminescence energies 1.65 and 1.53 eV are similar in shape and peak
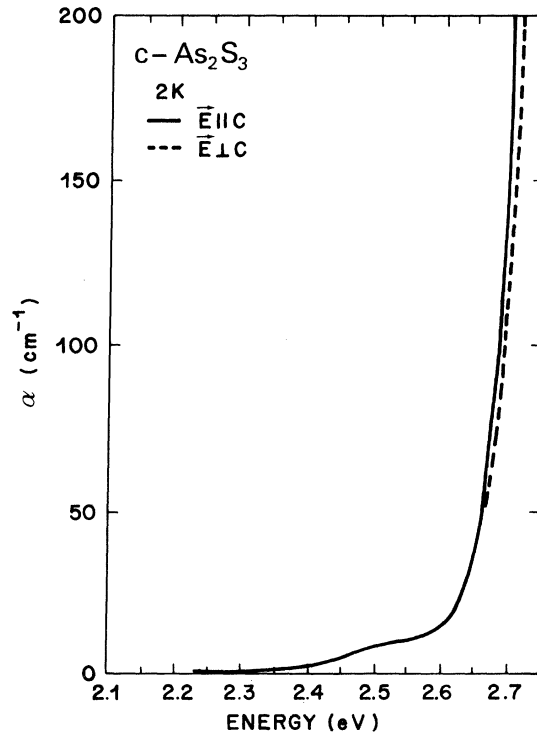

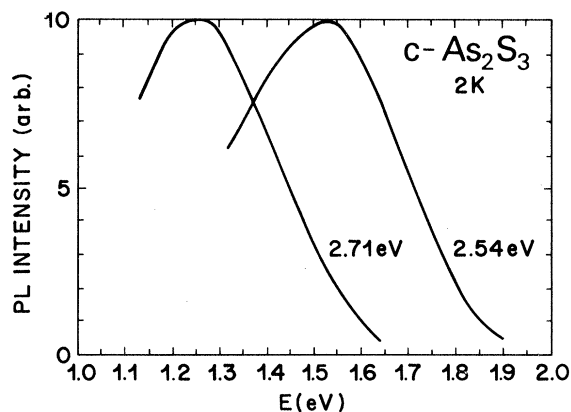FIG. 1. Optical-absorption tail spectra measured with polarized light at 2 K.

FIG. 2. Photoluminescence spectra of orpiment for two different excitation energies. (The luminescence is plotted in photons/cm^2 eV.)

around 2.58 eV with a half-width of 0.2 eV. Notice that the peak luminescence excitation spectrum is in good agreement with the published data.[3] The position of these excitation spectra corresponds closely to the absorption band in the tail region. The high-energy luminescence may originate from excitations between the band edge and a shallow impurity band. On the other hand, the third excitation curve for the luminescence at 1.39 eV increases monotonically with increasing excitation energy (with further increased excitation energy the curve will flatten out and even-
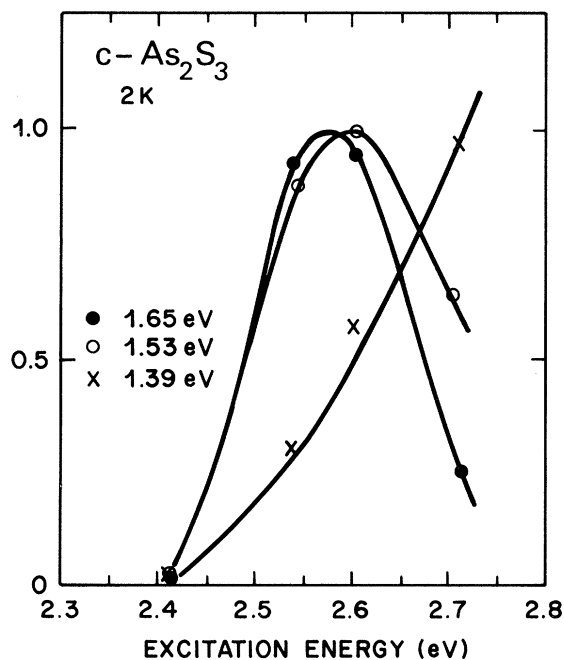
tually decrease). It is apparent that the low-energy luminescence originates from the onset of band-to-band transitions.

We discuss first the high-energy luminescence, which can be assigned to a defect-related process. The excitation from a band edge to a shallow impurity level produces localized electron-hole pairs bound at the impurity. These bound excitons predominantly recombine radiatively without ionizing into the band at low temperature. If bound excitons are ionized, high-energy luminescence would not occur since these electron-hole pairs would contribute to the recombination channel leading to the lower-energy luminescence discussed later. The larger Stokes shift of the high-energy luminescence is considered to be due to strong exciton-phonon coupling. The configurational coordinate diagram shown in Fig. 4 describes the excitation and recombination process invoking a bound exciton localized at an impurity. Excitation to B is followed by relaxation into the bound-exciton state. This is accomplished by displacement of atoms through electron-phonon interaction. Radiative recombination of the bound exciton is then responsible for the observed emission with the large Stokes shift. We calculate now the line shape of the luminescence band. The harmonic adiabatic potentials for the ground and the bound-exciton state can be approximately written as[7]

$$E_g(Q) = aQ^2 \ , \tag{1}$$

$$E_{ex}(Q) = aQ^2 - bQ + E_x \ , \tag{2}$$

where Q represents the configurational coordinate. The energy difference at $Q = 0$ is given by E_x. The

FIG. 3. Photoluminescence excitation spectra of orpiment. (The curves are normalized.)
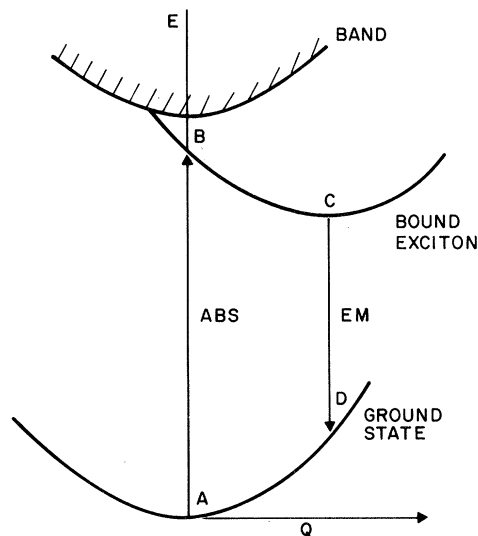

FIG. 4. Frank-Condon diagram for the bound-exciton process.

parameter a for the harmonic potential is related to the vibrational mode by

$$a = M\Omega^2/2 \ . \tag{3}$$

M is an effective mass of the phonon mode and Ω is the vibrational frequency. The constant b is a measure of the coupling strength between exciton and phonon. In this case, the Frank-Condon shift is given by

$$S = b^2/2a \ . \tag{4}$$

The line shape of the absorption and luminescence band is Gaussian, and the half-width is

$$\delta = [4(\ln 2)S\hbar\Omega]^{1/2} \ . \tag{5}$$

Using an average vibration energy of $\hbar\Omega = 350$ cm^{-1} and $S = 1.01$ eV, we calculate $\delta = 0.35$ eV. Although this linewidth is in close agreement with the experimental value, this simplified model is not specific to a bound exciton. Nevertheless, it is reasonable to assume that this luminescence band is due to the recombination of a bound exciton interacting strongly with phonons, since the absorption and excitation spectra indicate a narrow impurity band and that a large Stokes shift is occurring.

We have pointed out already that band-to-band excitation induces a low-energy photoluminescence band. This emission is characterized by very large Stokes shift and large half-width of the spectrum. Three types of models for this low-energy luminescence band can be considered. They are based on the recombination from: (i) deep recombination centers, (ii) donor-acceptor pairs, and (iii) self-trapped excitons. We briefly mention the first two models and describe in more detail the third possibility.

Kolomiets *et al.*[1] suggested a radiative-recombination process via deep-lying levels inside the gap. Street *et al.*[3] refined the deep-center model by invoking electron-phonon interaction to account for the large Stokes shift and linewidth.

Luminescence from donor-acceptor pairs was studied extensively for doped semiconductors.[8] Electrons and holes excited by band-to-band transitions are trapped at the corresponding defects. These trapped carriers can then relax and radiatively recombine. The donor-acceptor-pair model is less likely to be applicable since the low-energy luminescence is more or less invariant for natural orpiment samples of very different origins.

A self-trapped-exciton model has been proposed by Bösch *et al.*[4] to account for the luminescence dynamics in orpiment. To explain the low-energy luminescence, very severe localization is required. The following model is based on the *a priori* assumption of localization of the electron or hole wave function in the crystal. This is conceivable, since orpiment is a molecular-type crystal with weak interlayer bonding. We suppose that optical excitation over the band gap creates an electron and hole correlated in an exciton state. Rapid localization of the electron wave function due to the particular bonding configuration of orpiment can take place with subsequent small polaron formation (strong electron-phonon interaction). The hole still has a high mobility but is moving in the Coulomb field of the electron. Close to the Coulombic center the hole can be induced to localize and, if it overcomes the barrier to self-trapping, a severely self-trapped exciton is formed. Photoluminescence with a large Stokes shift may then be understood by radiative recombination of this localized exciton.

In summary, we have observed two steady-state photoluminescence processes in orpiment at low temperature. The emission at 1.53 eV is excited by an optical transition in an impurity band at 2.58 eV and is assigned to a defect-related bound-exciton recombination. The low-energy luminescence process is attained by band-to-band transitions and can be explained by the self-trapping of an exciton. Time-resolved luminescence studies will be necessary to evaluate the consistency of the proposed model.

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