[10] P. O. Hedén, H. Löfgren, and S. B. M. Hagström, Phys. Rev. Lett. 26, 432 (1971).

[11] Various possible sources of spurious satellite structure were investigated. The emission spectrum of the Al x-ray anode was found to be free of measurable impurity emissions. Runs with a blank sample holder and with bare tape gave no lines in the region of interest. Various other binding energy regions of the sample were scanned. The only impurity found was carbon. This absence of other impurities is consistent with the chemical analyses of the materials used.

[12] C. E. Moore, *Atomic Energy Levels as Derived from Analyses of Optical Spectra,* National Bureau of Standards Circular No. 467 (U.S.G.P.O., Washington, D. C. 1949), Vol. I.

[13] M. O. Krause, T. A. Carlson, and R. D. Dismukes, Phys. Rev. 170, 37 (1968).

[14] R. S. Crisp, Phil. Mag. 5, 1161 (1960).

[15] D. W. Fischer and W. L. Baun, Anal. Chem. 37, 902 (1965).

Photoluminescence of Amorphous $2As_2Te_3 \cdot As_2Se_3$ Films

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The photoluminescence of amorphous $2As_2Te_3 \cdot As_2Se_3$ films has been measured from 2 to 150°K with niobium-doped yttrium aluminum garnet laser excitation. The external quantum efficiency is estimated to be 20 %. A typical spectrum consists of a broad band peaked at 0.61 eV with a half-width of 0.15 eV. The energy value for the luminescence peak supports the concept of a recombination gap in amorphous semiconductors.

On first thought luminescence seems to be highly unlikely in amorphous semiconductors: Though the existence of optical[1-5] and mobility[6,7] gaps is well established, at least for chalcogenides, the theory favors a continuum of states throughout the gap.[5-7] Thus, an electron excited into the conduction band is expected to give up its energy not by radiative recombination but rather by jumping down the continuum of states, by emitting phonons. In spite of that, photoluminescence has been found from bulk samples of amorphous $As_2Se_3 \cdot As_2Te_3$, As_2Se_3, and As_2S_3.[8,9] These luminescence spectra had maxima well below the forbidden gap and were attributed[8,9] to transitions to impurity-like levels within the quasiforbidden gap.

In this paper we present measurements of the photoluminescence from amorphous films of $2As_2Te_3 \cdot As_2Se_3$ and interpret the spectrum in terms of simultaneous radiative recombination and phonon emission in a continuum of states. We also give the first results for amorphous films and the first results on the temperature and excitation intensity dependence of the spectrum. We chose $2As_2Te_3 \cdot As_2Se_3$ since measurements of its photoconductivity[10] had led to the introduction of a new kind of gap for an amorphous semiconductor. The photoconductivity, though yielding two well-defined activation energies, could be explained on the basis of a continuous density of states throughout the forbidden gap by introducing recombination edges about 0.2 eV below the mobility edges.[10-12] Above the recombination edges, relaxation of excited carriers is more probable than recombination, and vice versa below the edges.[10] In consequence, the states below the recombination edges are not expected to be strongly populated with carriers created by incident light.

Experiment and results.—The films used were 0.5 to 1.0 μm thick and were obtained by electron beam heating of bulk material and condensing the vapor on sapphire substrates cooled to 77°K. The 1.06-μm radiation of the niobium-doped yttrium aluminum garnet (Nd:YAG) laser was chosen for excitation. Light of this wavelength penetrates about 0.4 μm into the sample,[13] far enough to keep surface effects low, but allowing a good fraction of the incident light to be absorbed. The area of the illuminated spot on the sample was about 4 mm^2, and laser intensities up to 400 mW were used. The luminescence was analyzed through a LiF prism monochromator with an effective slit width of about 0.04 eV at 0.6 eV, and detected by a PbS cell at ambient temperature. The laser was typically chopped at 80 Hz. No difference in the signal was found when the chopping frequency was reduced to 13 Hz, which indicates that all detectable recombinations occur in a time much less than 10 msec. The excitation intensity was varied by calibrated metal-film filters. For measure-

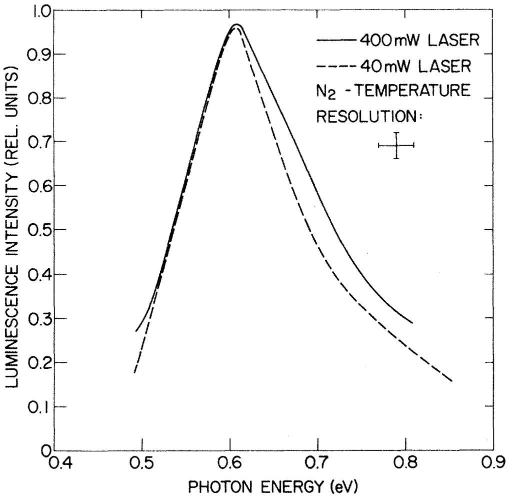

FIG. 1. Luminescence spectrum of amorphous $2As_2Te_3 \cdot As_2Se_3$ films for two different excitation intensities. The noise level is indicated by the vertical error bar.

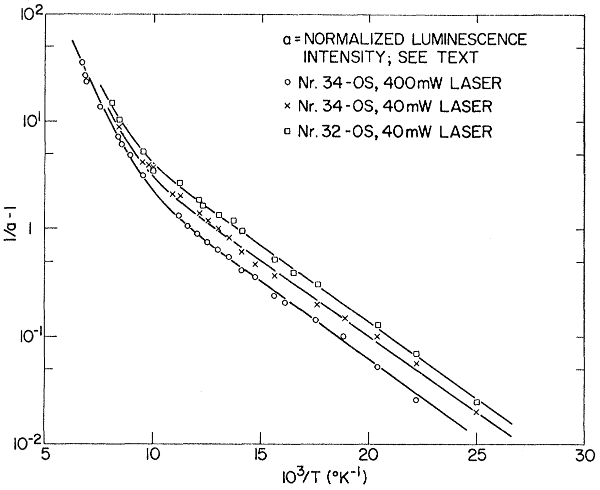

FIG. 2. Dependence of luminescence intensity on temperature. The data are plotted as $\log(1/a-1)$ vs $10^3/T$ to show activation energies of competing processes.

ments below 4.2°K the samples were immersed in liquid helium. A cold-finger Dewar was used for higher temperatures. The samples were attached to the copper block with gallium and additionally held with clamps.

The luminescence spectrum at 77°K is shown in Fig. 1 for two different levels of excitation. The measurements were restricted at high energy by filters which cut off the laser line and at low energy by the low sensitivity of the PbS cell. For both excitation levels the low-energy tails of the normalized spectra look the same, but the high-energy tail is enhanced at high excitation intensities. The energy of the maximum remains fixed within experimental error. At excitation levels lower than about 50 mW the shape of the spectrum does not change with intensity. The shape of the spectrum was also independent of temperature in the range in which it could be investigated (2 to 110°K), and was found to be reproducible from sample to sample.

The integrated luminescence intensity was found within experimental error to rise linearly with excitation intensity as the excitation intensity was varied by a factor of 50.

Preliminary measurements of the external quantum efficiency, uncertain by a factor of about 2, yielded a value of 20% at 4°K. The integrated intensity $I(T)$ of the luminescence is constant up to 40°K and then gradually decreases until it reaches about 2% of the initial value at 150°K. This dependence is shown in Fig. 2 and plotted as $\log(1/a-1)$ vs $10^3/T$, where $a(T)=I(T)/I(0)$ and T is the absolute temperature. A plot of this kind is suggested if we assume that the internal quantum efficiency is unity at 0°K and that there is a competing nonradiative process with activation energy ϵ. If the competing normalized rate is b, then

$$a+b=1, \tag{1}$$

$$b=afe^{-\epsilon/kT}, \tag{2}$$

and thus

$$1/a-1=fe^{-\epsilon/kT}. \tag{3}$$

f is a proportionality factor related to the transition probability for the competing process. Figure 2 shows that Eq. (3) describes our results below 100°K with an ϵ of 30 meV. The whole curve including the rise at higher temperatures can be fitted very well by an expression with a second competing process with an activation energy of 100 meV. The physical nature of these competing processes is still subject to speculation. One such process might be the diffusion of carriers to the surface with subsequent nonradiative recombination.[14] From the linear dependence of the luminescence on excitation intensity at 77°K one can conclude that the luminescence and the competing process with 30-meV activation energy must obey recombination kinetics of the same order.

Model.—We now consider a model,[10] illustrated in Fig. 3, which can account for a peak in the luminescence spectrum at an energy well below

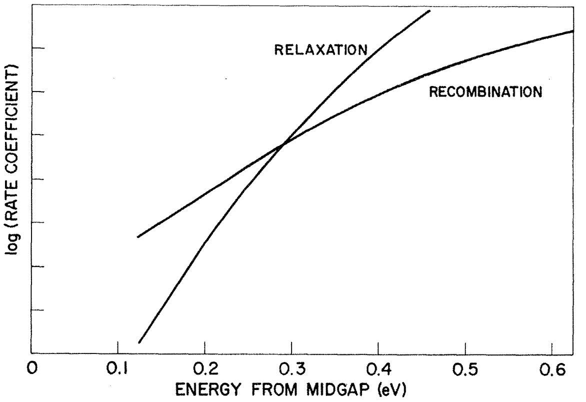

FIG. 3. Qualitative plot of the relaxation- and recombination-rate coefficients versus energy from midgap. The recombination edge E_R lies near the crossover.

the energy of the optical and conductivity gaps. We suppose that carriers are injected optically at energies near or above the mobility edges, and that they subsequently relax to lower energies by phonon emission at a rate r_{rel} while at the same time electrons and holes are recombining at a rate r_{rec}. Both the relaxation-rate coefficient and the recombination-rate coefficient are expected to decrease as the density of states decreases and the states become more localized, but the latter is expected to vary more slowly because localized carriers can recombine with carriers in extended states in the other band. The peak of the resulting carrier distribution is expected to lie near the crossover of these two rates.

We now solve the rate equations for a simple version of this model: We assume that the energy relaxation takes place only by phonon emission (i.e., at absolute zero) and that only a single phonon energy E_{ph} is involved. Furthermore we ignore the energy dependence of the recombination coefficient in Fig. 3 and take the radiative recombination rate to be independent of the energy of the initial and final states. We also assume that the conduction and valence bands have identical properties, and ignore the equilibrium carrier concentration.

Under these simplifying assumptions, the rate equations are

$$\dot{n}_i = t_{i+1} n_{i+1} + g_i - t_i n_i - B n_i n, \qquad (4)$$

where n_i is the carrier concentration of level i, n $(=p)$ is the total carrier concentration, $t_i n_i$ is the rate at which carriers in level i emit phonons to drop to level $i-1$, g_i is the excitation rate per unit volume into level i, and Bn is the radiative recombination-rate coefficient. The energies of successive levels differ by the phonon energy E_{ph}. The steady-state solution of these equations can be written down by inspection if we assume that all the carriers are injected into level j, which lies well above the recombination edge. Then

$$n_j = G/(t_j + Bn), \qquad (5a)$$

$$n_i = n_{i+1} t_{i+1}/(t_i + Bn), \qquad (5b)$$

where G is the total excitation rate. The total steady-state carrier concentration n is $(G/B)^{1/2}$.

The carrier distribution will peak near the energy for which $t_{i+1} \sim t_i + Bn$. If the thermalization rate increases as $\exp(E/E_t)$ in the energy range of interest, then the peak lies near the energy for which the thermalization-rate coefficient is

$$t \sim Bn/2\sinh(E_{\mathrm{ph}}/2E_t). \qquad (6)$$

The half-width of the distribution is approximately $4E_t$.

Figure 4 shows the carrier distribution and the resulting emission spectrum obtained from (5) with $E_t = 30$ meV, $E_{\mathrm{ph}} = 25$ meV, $t(0.3\ \mathrm{meV}) = 10^6\ \mathrm{sec}^{-1}$, $B = 5\times10^{-11}\ \mathrm{cm}^3\ \mathrm{sec}$, and $G = 10^{22}\ \mathrm{cm}^{-3}\ \mathrm{sec}^{-1}$. The spectrum is independent of the ratio $t/(GB)^{1/2}$, and its shape is not strongly dependent on E_{ph}.

Discussion. —The measured luminescence peak is at 0.6 eV, just where it would be predicted on the basis of the recombination edge model proposed to explain the photoconductivity measurements in these films.[10] The more quantitative, although highly simplified, model presented here can explain the observed peak, but is in disagreement with experiment in one important re-

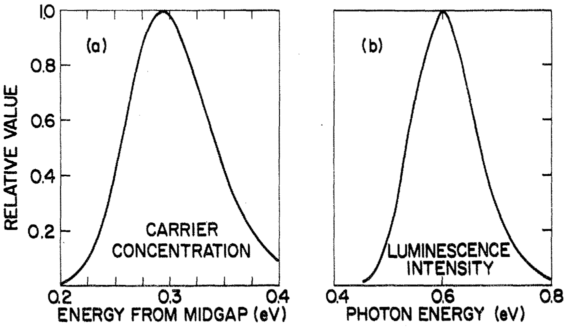

FIG. 4. (a) Steady-state electron (or hole) distribution versus energy from midgap, and (b) emission spectrum versus photon energy, calculated from the simple model leading to Eq. (5).

spect. The relation (6) for the peak of the carrier distribution, together with the square-root relation between carrier concentration and excitation rate given above, implies that the carrier distribution peak shifts by $1.15E_t$ when the excitation rate G changes by a factor of 10. The emission spectrum shifts approximately twice as fast. Thus the predicted shift of the peak for a tenfold increase in intensity is about 70 meV, while the observed shift is at most 15 meV, which is half of the shift of the high-energy tail in Fig. 1. We have considered more general rate equations, but have not yet resolved the inconsistency with the experimental results.

The discrepancy between the large observed linewidth and the small peak shift could be due to line-broadening mechanisms not considered in our model. Sample inhomogeneity on a small scale compared to the light-spot size may be a factor. Coulomb interaction between the localized electrons and holes[15] may also contribute to the width of the observed spectrum. Peaks in the density-of-states tails[5,16] about 0.2 eV from each mobility edge could help to account for the absence of a peak shift.

We conclude that the luminescence peak is consistent with the notion of a recombination edge as proposed in connection with photoconductivity measurements,[10] although complete quantitative agreement has not yet been achieved. Experiments on other materials and on the time dependence of the luminescence should provide further information on the thermalization and recombination processes in amorphous semiconductors.

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[1] J. Tauc, R. Grigorovici, and A. Vancu, Phys. Status Solidi 15, 627 (1966).

[2] K. Weiser and M. H. Brodsky, Phys. Rev. B 1, 791 (1970).

[3] W. E. Howard and R. Tsu, Phys. Rev. B 1, 4709 (1970).

[4] A. E. Owen and J. M. Robertson, J. Non-Cryst. Solids 2, 40 (1970).

[5] E. A. Davis and N. F. Mott, Phil. Mag. 22, 903 (1970).

[6] N. F. Mott, Phil. Mag. 22, 1 (1970).

[7] M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, Phys. Rev. Lett. 22, 1065 (1969).

[8] B. T. Kolomiets, B. T. Mamontova, and A. A. Babaev, Phys. Status Solidi 27, K15 (1968).

[9] B. T. Kolomiets, B. T. Mamontova, and A. A. Babaev, J. Non-Cryst. Solids 4, 289 (1970).

[10] K. Weiser, R. Fischer, and M. H. Brodsky, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U.S. AEC Division of Technical Information, Springfield, Va., 1970), p. 667.

[11] A similar model was proposed by W. E. Howard and R. Tsu, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970,* edited by S. P. Ketter, J. C. Hensel, and F. Stern, CONF-700801 (U.S. AEC Division of Technical Information, Springfield, Va., 1970), p. 789.

[12] The "thermalization edge" found by drift experiments in amorphous Si by P. G. Le Comber and W. E. Spear, Phys. Rev. Lett. 25, 509 (1970), can be interpreted in a similar manner.

[13] M. H. Brodsky and G. D. Pettit, unpublished.

[14] D. Kaplan and M. I. Nathan, private communication

[15] M. Pollak, Discuss. Faraday Soc., No. 50 (1971).

[16] M. H. Cohen, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern, CONF-700801 (U.S. AEC Division of Technical Information, Springfield, Va., 1970), p. 645