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[15]The possibility for a quadrupolar phase transition preceding a dipolar one was proposed by P. M. Levy and H. H. Chen [Phys. Rev. Lett. 27, 1385 (1971)] for the pnictides but they were subsequently found not to exhibit separate transitions.

[16]Removing the linear Jahn-Teller coupling from the Hamiltonian for a cubic system by using the displaced-oscillator technique runs into difficulties when there are noncommuting operators. In these cases, R. J. Elliott [*Proceedings of the International Conference on Light Scattering in Solids, Paris, 1971*, edited by M. Balkanski (Flammarion Press, Paris, 1971), p. 354] and Gehring and Gehring (Ref. 2) have shown that one can approximately remove the coupling by a unitary transformation. The sign of I_θ, Eq. (3), will nonetheless be negative.

[17]See Ref. 4, Eq. (2).

[18]The outer closed shells ($5s^2 5p^6$) normally reduce the quadrupole moment and the coupling while the open-shell electrons, especially the $5d$, increase it. When we consider the outer $5d, 6s$ electrons itinerant, they mediate an indirect coupling of the quadrupoles (see next paragraph in text). The sign of this indirect coupling can be positive.

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Band-to-Band Luminescence in Amorphous Solids: Implications for the Nature of Electronic Band States

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The observation of band-to-band luminescence from an amorphous solid (a-As_2S_3) shows the existence of localized states at energies considerably above the mobility edge.

The true nature of the electronic states in amorphous solids continues to be a subject of intense investigation. Anderson[1] showed that the electronic states in a disordered system are localized for the case of strong disorder. It was proposed[2,3] that the disorder in amorphous solids is not sufficiently strong so that localization occurs only near the extremities of the band and a sharp transition[3] from localized to extended states occurs at an energy called the mobility edge. Most of the evidence for this picture has come from electronic transport properties. Luminescence from band states would provide direct information about them; however, only sub-bandgap luminescence has been reported.[4-6]

We report in this Letter the first observation of band-to-band luminescence in an amorphous solid. This luminescence process has many novel properties. The luminescence spectrum extends to photon energies much higher than the bandgap energy E_0 deduced from optical absorption measurements. This spectrum shifts to higher energy as the excitation energy $h\nu_{ex}$ is increased and the peak of the spectrum occurs at an energy greater than E_0 for the highest excitation energy. We also observe for the first time anti-Stokes luminescence, i.e., luminescence at energies higher than $h\nu_{ex}$. If this band-to-band luminescence is attributed to recombination of free electrons and holes, we conclude from the data that these free carriers are not thermalized, in contrast to what would be expected for truly extended states. The results are discussed in terms of geminate recombination and Frenkel-type exciton. Knowledge of the nature of the electronic band states (electronic states in the valence and conduction bands) of amorphous semiconductors is essential in understanding many

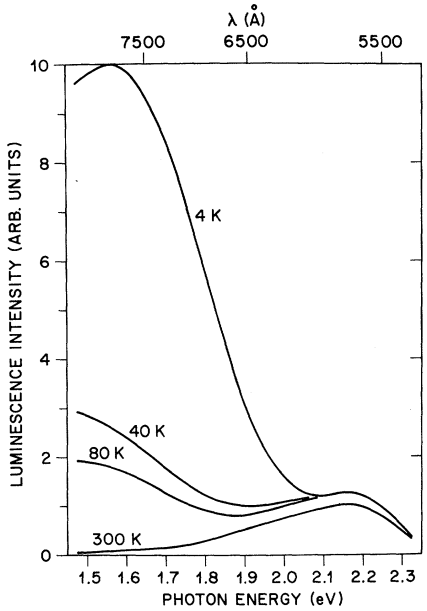

FIG. 1. Luminescence spectra of a-As_2S_3 at different temperatures for an excitation wavelength of 5145 Å. Spectral resolution is 30 Å and the intensity is in units of photons per second.

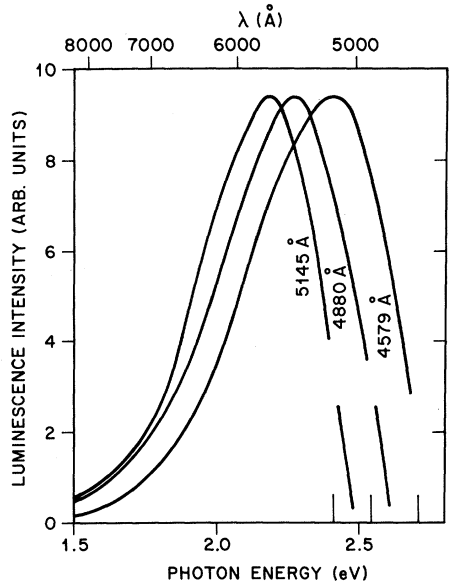

FIG. 2. Luminescence spectra of a-As_2S_3 for different excitation wavelength at 300 K. The Raman lines at $\approx$180 and 340 cm^{-1} are suppressed for clarity.

properties of these materials. Band-to-band luminescence provides direct information about these processes and should prove to be a unique and important probe for a detailed investigation of these states.

Different samples of amorphous As_2S_3 with optical-grade polish have been investigated in the temperature range from 2 to 300 K. The sample was excited by a focused (0.1×3 mm^2) argon-laser beam. The argon laser was cavity dumped to provide 11-nsec pulses at 30-kHz repetition rate; the incident average power was 0.5 mW to minimize fatigue and avoid damage. The luminescence was collected from the excited face and dispersed by a double spectrometer (extreme care was taken to minimize the amount of scattered laser light entering the spectrometer) and detected by a photomultiplier with GaAs photocathode and a photon counter with a 20-nsec gate coinciding with the laser pulse.

Figure 1 shows the luminescence spectra at four different temperatures for 5145-Å excitation wavelength. The dominant emission band at 4 K is located at $\approx$ 1.6 eV. We have shown earlier[7] that the low-temperature luminescence spectrum of a-As_2S_3 excited by short pulses consists of two peaks [due to a low-energy process (LEP) and a high-energy process (HEP)]. In the present experiment we have used 20-nsec time resolution with the result that the LEP and HEP have merged into a single band peaking at 1.6 eV. The present results show that in addition to this band, the spectrum at 4 K has a broad subsidiary peak at $\approx$ 2.2 eV. With increasing temperature the 1.6-eV band diminishes in intensity whereas the 2.2-eV band remains unchanged with the result that two peaks of comparable amplitudes are observed at 80 K. The 1.6-eV band has completely disappeared by 200 K and the spectrum is dominated by the 2.2-eV band. The intensity of the 2.2-eV band remains approximately constant up to 200 K and decreases by $\approx$ 20% between 200 and 300 K. At all temperatures investigated, the 2.2-eV luminescence band decays faster than our time-resolution capability of 10 nsec.

The room-temperature luminescence spectra for three different excitation wavelengths are shown in Fig. 2. The spectrum shifts to higher energy as the excitation photon energy is increased. The shift in the spectrum is approximately 2/3 of the change in the excitation photon energy. The shape of the spectrum does not change appreciably with excitation wavelength. Note that the emission extends as much as 0.4 eV above the optical bandgap of 2.32 eV deduced from absorption measurements,[8] and that the peak of the luminescence occurs above this energy for 4579 Å excitation. For these reasons, we have called this emission band-to-band lumines-

cence. An interesting feature of the room-temperature spectra is the presence of the anti-Stokes emission, i.e., emission of photons with energy higher than the energy of the exciting photon. This anti-Stokes emission diminishes in intensity with decreasing temperature and disappears completely at 4 K.

Electronic Raman scattering is not a viable interpretation of the data because the observed peak shifts less than the shift in the excitation energy (Fig. 2). Furthermore, the possibility of Raman scattering from photoexcited carriers is also ruled out since only linear dependence on excitation intensity is observed.

We discuss these results first in terms of the concept of mobility edge proposed by Mott.[3] According to this model the electronic states in the tails of the bands are localized up to a certain well-defined energy called the mobility edge beyond which the states are extended. The carriers excited into the extended states would be expected to thermalize rapidly to the mobility edges and the only emission expected above the mobility gap (E_g) would be due to a thermal tail of the carrier distribution and would have the form $\exp[(E_g - E)/kT]$. Our data do not show this thermal tail and extend to energies much higher[9] than $E_g \approx 2.4$ eV. Furthermore, the luminescence spectrum shifts with excitation photon energy and the peak of the spectrum for the 4579 Å excitation is even higher than the mobility gap. We therefore conclude that the thermalization time of photoexcited electrons or holes or both is longer than their lifetime. This implies that these band states are at least partially localized and this localization impedes rapid thermalization of carriers.

If the states in both the valence and conduction bands are localized, or if the mean free paths of carriers are very short as expected for an amorphous semiconductor, the probability for the recombination of an electron and a hole produced by different photons would be very small due to their spatial separation. An alternative concept would then be geminate recombination, where recombination occurs only between the electron and the hole created by the same photon. The observed emission band peaking at a lower energy compared to the excitation photon energy would be explained by either simultaneous emission of a photon and phonons or more probably by the emission of a photon from a relaxed pair. Since the carrier-lattice interaction is strong in these solids, it is likely that one of the particles (probably the hole) of the geminate pair interacts strongly with the lattice and becomes dressed.[10] The electron would then be attracted by the Coulomb field of the dressed hole and the recombination of this complex is responsible for the observed emission.

Sub-bandgap luminescence is explained predominantly within two defect models. Street and Mott[11] have introduced the idea of unoccupied, singly or doubly occupied defect states at dangling bonds. Kastner, Adler, and Fritzsche[12] deduce the properties of defect centers from the chemical bonding. These models involve localization and lattice relaxation at a defect and as such are not specifically applicable to the proposed explanation of an electron in the Coulomb field of a dressed hole as proposed above. More recently Kastner and Hudgens[13] proposed the existence of excited defect states in resonance with electron-hole states in the bands. It is not clear at present if such states play any role in the observed luminescence.

The formation of an exciton is also a possible explanation for the band-to-band emission. This exciton would be resonant with the electron and hole states in the bands and is visualized as a localized excitation at atomic clusters.[14] Autoionization of this resonant exciton into electrons and holes is inhibited by distortions of the atomic clusters on which excitons are localized.

Several decay channels are possible for the excitation which gives rise to the observed band-to-band luminescence. The excitation can be self-trapped and decay nonradiatively,[15] or it may ionize into free carriers. The free carriers may subsequently form small polarons[16] or be trapped at defects, and generate the sub-bandgap luminescence which dominates at low temperature.

In summary we have presented data on band-to-band luminescence which manifests many novel properties including anti-Stokes emission. We have discussed these data in terms of the concepts of mobility edge, geminate recombination and exciton. We conclude that the electronic states in the bands are at least partially localized.

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Sliding-Mode Conductivity in $NbSe_3$: Observation of a Threshold Electric Field and Conduction Noise

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Two new effects associated with Fröhlich sliding-mode conductivity have been observed in $NbSe_3$. First, nonlinear resistance is observed only after a well-defined threshold field is reached. Second, electric fields above the threshold result in noise in the potential difference across a current biased specimen. We interpret the threshold field as direct evidence of charge-density wave depinning and the noise as a result of charge-density wave motion.

$NbSe_3$ is characterized by two independent charge-density wave (CDW) transitions, at 144 and 59 K.[1-3] As is characteristic of materials with CDW, large increases in the resistance are observed at temperatures below the two phase transitions.[1] $NbSe_3$ is thus far unique among this class of materials in that the extra resistivity associated with the CDW onset may be suppressed with very modest electric fields.[4] An empirical field-dependent conductivity has been written as[4,5]

$$\sigma(E) = \sigma_a + \sigma_b \exp(-E_0/E). \quad (1)$$

It is reasonable to associate the conductivity gained by the application of the electric field with a current-carrying CDW. The possibility of such a "sliding-mode" CDW was first proposed by Fröhlich[6]; however, recent theoretical considerations indicate that an incommensurate CDW in three dimensions is always pinned at zero field.[7-9] The model of a CDW which may be depinned by an electric field is now supported by both theory[10-12] and experiment.[3,5,13] In particular, it has been shown that the CDW amplitude is unaffected by electric fields which suppress over half of the 59-K resistive anomaly.[3] Recent resistivity measurements suggest that E_0 is a function of sample purity[3,13] and that E_0 varies as the square of the impurity concentration.[13] Microwave absorption[5] below 59 K indicates a local, field-induced phase slip of the CDW.

In this Letter we report the observation of two new effects associated with sliding-mode conductivity in $NbSe_3$. First, sliding-mode conduction only takes place when a well-defined threshold field, E_T, is reached. Second, as the electric field is increased above threshold, an abrupt increase in noise appears in the potential difference across a specimen. For slightly higher fields, discrete frequencies with high harmonic content can be detected in addition to the noise. The first effect requires that Eq. (1) be modified

