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Free-exciton confinement by layer stacking faults in GaSe: Evidence from time-resolved spectroscopy

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Picosecond photomodulation techniques have been applied to study the kinetics of the $n=1$ free exciton in the layered semiconductor GaSe. We have observed a lack of spectral diffusion within a stochastic inhomogeneous exciton resonance at low temperatures and use this to support arguments for partial exciton localization by layer stacking faults.

In recent years there have been suggestions that the random structure which is commonly seen in optical absorption, reflectance, or photoluminescence spectra in the $n=1$ direct free-exciton region in GaSe has an origin in partial confinement effects induced by stacking faults in this layered semiconductor.[1,2] These arguments note how the details of this substructure, which appear to be particularly pronounced in the case of one dominant layer polytype, are usually sample and thickness dependent in a rather stochastic way but bear little evident connection to the impurity content. In particular, Fourney, Masche, and Mooser[1] have outlined a model for exciton confinement effects by adding a weak aperiodic perturbation to the free-exciton Hamiltonian and estimated that the average confinement occurs in a fault-induced "channel" of some 15 layers thick.

In this Rapid Communication we present results of the $n=1$ free-exciton kinetics by time-resolved photomodulation spectroscopy on a subnanosecond time scale in thin platelets of GaSe. The main emphasis in this work has been to look for spectral diffusion within the evidently inhomogeneous $n=1$ transition at different temperatures. As we show below, our results can be used to provide support to the ideas of weak localization of the free exciton by layer potential barriers on the order of 1 meV, randomly distributed in the samples. In addition, we have seen inhomogeneous effects in the bound exciton kinetics as well. Because of the stochastic aspect of the problem, however, the interpretation of our results is made primarily through semiquantitative arguments.

The experiments were carried out on platelets of GaSe, cleaved from good quality single crystals perpendicular to the c axis. The absorption spectra on thin platelets (5 μm and less in thickness) displayed pronounced fine structure over an approximately 10-meV range of the direct $n=1$ exciton and had a generally random character with little correlation between different platelets, particularly at low temperatures. Figure 1 shows a measured absorption spectrum in this region (centered about 2.110 eV) under moderate resolution (0.4 meV) on a sample at $T=1.8$ K, for optical polarization perpendicular to crystal c axis. This polarization corresponds to a weakly allowed transition where polariton effects are unimportant. Earlier, LeChi, Depeursinge, and Mooser,[3] among others, have reported strong substructure within the $n=1$ exciton over a spectral width of approximately 10 meV.

The time-dependent studies were performed by using a pair of synchronously pumped, mode-locked dye lasers in an excite-probe mode. Because of efficient signal averaging the arrangement gives high-amplitude sensitivity so that weak excitation can be employed to perform picosecond photomodulation spectroscopy, with excitonic densities far below the Mott transition. Previously, we have applied this technique to the study of kinetics of free carriers, free excitons, and impurity bound excitons in a number of semiconductors.[4] In the experiments, the excitation promoted by a picosecond pump pulse is "read out" as a fractional change in transmission of a probe pulse (dT/T), and the resultant photomodulated spectrum can be constructed for a variable range of time delays. Typical excitonic densities are 10^{14} cm^{-3}, usually well below the Mott transition for free excitons and below saturation for localized excitons. In the case of an isolated, homogeneously broadened free-exciton resonance, a characteristic spectral line shape is expected, assuming a model where exciton-exciton collisions modulate both the linewidth and the resonance frequency of a simple Lorentzian line-shape function. Neglecting the usually small contributions to the index of refraction (which can become important for very narrow exciton resonances), we obtain for small photomodulated absorption:

$$dT/T = -d\alpha l = -\left(\frac{\partial\alpha}{\partial\Gamma}d\Gamma + \frac{\partial\alpha}{\partial E_0}dE_0\right)l \ , \tag{1}$$

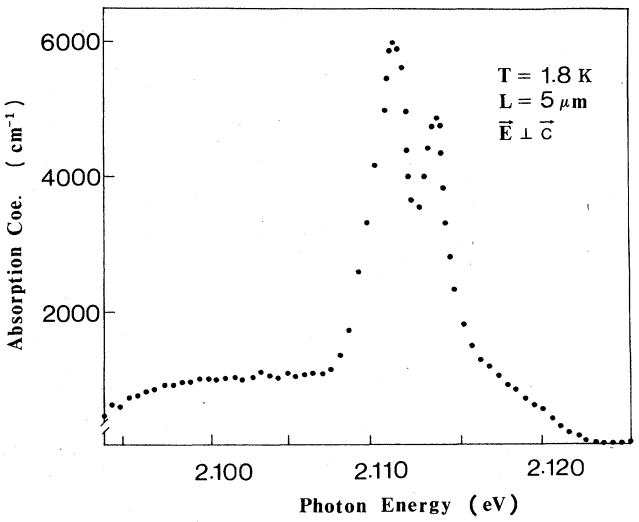

FIG. 1. Absorption coefficient in a 5-μm platelet of GaSe in the $n=1$ direct exciton region at $T=1.8$ K.

where Γ is the linewidth, E_0 the resonance energy, and l the sample thickness. In the case of Ge, Thomas *et al.*[5] were able to describe well such modulated spectra in steady-state experiments. [Recently, we have obtained very good quantitative agreement with this model and experiment from transient spectra of the yellow exciton series in Cu_2O (Ref. 6) by assuming that the collisional broadening term in Eq. (1) dominates over the induced shift of the resonance frequency.] The main qualitative consequence of this model is that the experimentally measured quantity dT/T undergoes changes of sign near E_0 in the case of free excitons. The details depend on the relative contributions of the two terms in Eq. (1). This is in contrast with the photomodulated spectra of bound excitons, for which dT/T remains positive (enhanced transparency) throughout the resonance.

Figure 2 shows time-resolved modulation spectra for three different delay times in the 5-μm-thick GeSe sample at 1.8 K, following the excitation by a picosecond pulse within the $n=1$ free-exciton region at $t=0$. (Optical interference effects have been subtracted automatically by our instrumentation, an easy task for samples in this range of thickness.) The time resolution in these experiments was approximately 15 psec. As expected from the absorption measurements, the photomodulated spectra shows appreciable structure. Measurements on several platelets brought out distinctly different structure for each, but the spectra were always characterized by a line shape which could be viewed as a superposition of a (small) number of simple resonances expected for free excitons [Eq. (1)], including the changes of sign in dT/T. We note again that while for a single, homogeneously broadened exciton resonance a photomodulated spectrum can be fitted with a calculated line shape with no adjustable parameters,[6] the platelet to platelet randomness encountered here makes a more detailed spectral analysis quite difficult. Thus, we make no further attempts to decipher the details of these spectra in this Rapid Communication, apart from identifying them with multicomponent free excitons with stochastic amplitudes.

The point which we wish to focus on here concerns the lack of spectral diffusion and the rather independent rates of amplitude decay which characterize the different portions of the spectra such as that in Fig. 2. A detailed examination of these spectra invariably showed the presence of a wide range of decay rates for different subcomponents on subnanosecond time scale (typically from less than 200 to over 500 psec). Our samples had an estimated background impurity density in the range of 5×10^{16}–1×10^{17} cm^{-3} and cw photoluminescence spectra showed a contribution from bound exciton emission by two main components centered at approximately 2.100 and 2.090 eV. Therefore, the observed decay of the free-exciton components must have a component from the formation of bound excitons. We also monitored the formation times of the bound excitons and seen a rough correlation between the faster rates of free-exciton decay and the bound exciton formation (more precise identification with individual free-exciton components could not be made since photomodulation measurements in the bound exciton region required another set of thicker samples for enhanced optical density).

As the photon energy of excitation varied throughout the $n=1$ free-exciton region, random spectra such as that in Fig. 2 with unpredictable component amplitudes were recorded but, for a given platelet, with a "center of gravity" which followed the energy of excitation. Again, apparently random rates of amplitude decay were seen in separate portions of the total spectrum at $T=1.8$ K. At higher temperature, however, distinctly different transient behavior became evident in the spectra. Specifically, at about and above 10 K, dynamic correlation appeared within the free-exciton line amongst the subcomponents. Figure 3 illustrates the point at $T=47$, K for the 5-μm-thick platelet where the exciton photomodulated spectrum has also acquired additional width and structure, most likely from sample strain related effects (phonon broadening alone seems insufficient). The lineshape details are not of primary importance for our arguments here, but what is noteworthy is that in this case a rather similar lifetime (about 2 nsec) is observed for the free-exciton components over its spectrum. Furthermore, clear evidence of spectral diffusion is seen during initial-energy relaxation on the time scale of some 200 psec. Note,

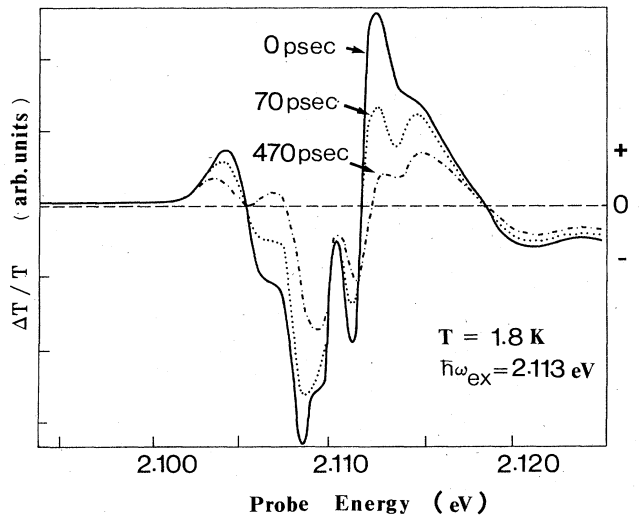

FIG. 2. Transient photomodulated spectra at 1.8 K, recorded 0, 70, and 470 psec following excitation at 2.113 eV.

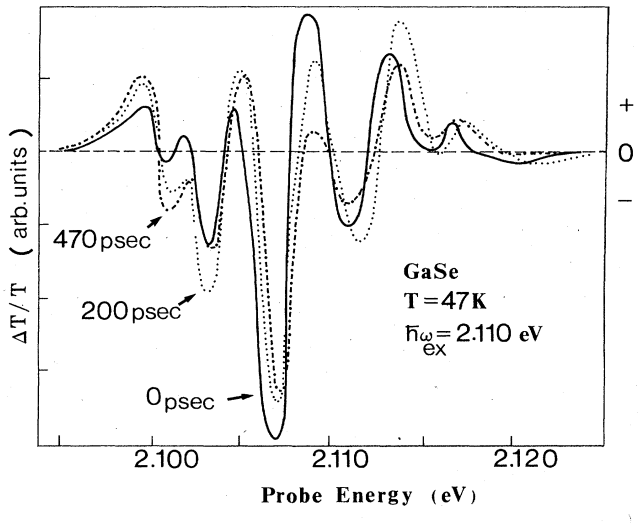

FIG. 3. Photomodulated spectra at 47 K, recorded 0, 200, and 470 psec following excitation at 2.110 eV, and showing the presence of spectral diffusion.

indeed, how in Fig. 3 amplitudes of components on both the high- and low-energy sides of the approximate spectral center (where injection of excitation occurred) continue to *grow* following the excitation while a monotonous decay occurs at the line center.

We consider these and similar observations on a number of thin platelets to yield direct support to the earlier arguments that a form of exciton localization occurs in GaSe by layer stacking faults for the $n=1$ direct free exciton. First, the photomodulated spectra (including the dependence on the photon energy of excitation) indicate an inhomogeneously broadened exciton line composed of a number of components of random amplitude and energy. The broadening here appears to be weak in the sense that the individual homogeneous component widths are of the order of the total inhomogeneous width. Our transient experiments clearly show the absence of any significant spectral diffusion within the exciton line at low temperatures, whereas strong diffusion is readily seen at elevated temperatures. In the context of the model of Fourney *et al.*,[1] where random stacking faults are considered to partially localize the $n=1$ exciton in a direction perpendicular to the layer planes, any spectral diffusion is identified by us with spatial diffusion in this direction. Random stacking, which can lead to a high concentration of stacking faults, is taken to be the origin for the stochastic envelopes of the inhomogeneous exciton line (both in the absorption and photomodulation spectra) and is reflected also in the lack of detailed sample to sample correlation. The concept of localization in Ref. 1 takes a free three-dimensional exciton in the effective mass approximation, assumes that the relative and center-of-mass (c.m.) motion can be decoupled, and considers an additional aperiodic perturbing potential (in c direction) to yield a schematic exciton wave function: $F(R,r)=f(R)g(r,R)$. In an adiabatic approximation, the finite coupling of the relative (r) and c.m. motion (R) in $g(r,R)$ gives a small modulation to the exciton internal energy through the stacking disorder potential, whereas the confinement effects follow from an equation of motion for the c.m.-envelope function $f(R)$. From the energy scale and range of the structure usually observed in absorption for the $n=1$ exciton transition in a thin platelet and the absence of such structure for the $n=2$ transition, a rough estimate can be made for the typical confinement distance in the c direction to be an average channel of less than 15 unit cell layers thick, or less than about 240 Å.[1] The Bohr radius of a spherical $n=1$ free exciton is estimated to be 80 Å in GaSe so that the confinement only slightly modifies the three-dimensional nature of the exciton (this, of course, is also consistent with the random spread of the $n=1$ exciton energies by only a fraction of the total binding energy of some 20 meV).

For the moderate impurity density in our (undoped) samples, a random distribution of impurities amongst such channels would imply that bound exciton formation rates (through free-exciton capture) be subject to random fluctuations in manner similar to the free-exciton inhomogeneous decay. We have seen strong inhomogeneous effects in the photomodulated bound exciton spectra at $T=1.8$ K on thicker samples, from which a mean-free-exciton capture time of roughly 150–200 psec can be clearly inferred. This time is comparable (and not significantly shorter) to the observed spectral diffusion time at higher temperatures. It suggests that energy relaxation to the low-energy side of the $n=1$ transition should also be observable at low temperatures, bound exciton effects not withstanding, if the process were allowed. In our interpretation, the observation of spectral diffusion only at higher temperatures is then consistent with the idea of thermally activated spatial diffusion of excitons perpendicular to confining stacking fault layers (the role of the bound excitons is now also being diminished from thermal dissociation arguments). From the observed temperature trends we estimate that the corresponding localization energy for the $n=1$ excitons is approximately 1–2 meV, in reasonable agreement with values extrapolated from the calculations of Fourney *et al.*[1] Finally, we wish to point out a similarity between these results and those obtained recently from studies of inhomogeneous exciton transport in multiquantum wells of GaAs/(Ga,Al)As.[7] In that work the fluctuation in well thickness was observed to lead to energy-dependent exciton diffusion.

In summary, we have presented experimental results by time-resolved spectroscopy which for the first time give a direct look at spectral diffusion and decay within the $n=1$ randomly broadened inhomogeneous exciton in GaSe. While the problem remains inherently statistical due to variations between samples and their thickness, and is not readily amenable for precise quantitative measurements, we have given new strength to the ideas that layer stacking faults in GaSe (in practice invariably controlled by external strain) are responsible for partial exciton localization in channels whose widths are on the order of the exciton Bohr diameter.

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