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CORE EXCITONS IN THE III-VI LAYERED SEMICONDUCTORS

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The problem of core excitons in semiconductors is not yet settled. As well known, large binding energies, E_b , (at least one order of magnitude larger than those of valence band excitons) are found for the core excitons, usually by comparing the energy $\hbar\omega_0$ of the first, sharp core structure with the sum of the fundamental gap energy, E_g , and the binding energy, E_d , of the core level with respect to the top of the valence bands: $E_b = \hbar\omega_0 - (E_g + E_d)$. Theories based on the effective mass approximation are not able to explain such large binding energies⁽¹⁾. Localized⁽²⁾ or dynamical⁽³⁾ models, instead, seem to work better. The latter is capable also to predict that the core exciton linewidth must be smaller than the photoemission core level linewidth. In a previous research on the III-VI layer compounds⁽⁴⁾, we have been puzzled by the fact that, in spite of the strong similarity between their reflectivity spectra and all their electronic properties, the binding energies of the core excitons associated with the Ga 3d transitions in GaS and GaSe (0.8 ± 0.3 eV and 0.4 ± 0.3 eV, respectively) changed significantly one from another and that the In 4d transitions in InSe did not have bound states. Thus we have measured the reflectivity spectra of the mixed compounds $\text{GaS}_{1-x}\text{Se}_x$ and $\text{Ga}_{1-x}\text{In}_x\text{Se}$ ($0 \leq x \leq 1$) in the energy region 17-25 eV, corresponding to the d excitation region, at several temperatures and with a resolution better than 15 meV. We measured also the photoemission spectra of the same samples, cleaved in ultrahigh vacuum, in order to determine with the same accuracy on all compounds the binding energy E_d of the Ga 3d and In 4d states. The measurements were performed using the vacuum ultraviolet and the photoemission beam lines of the Italian synchrotron facility PULS at the Frascati National Laboratories of the Istituto Nazionale di Fisica Nucleare.

From the photoemission spectra we found that the core level binding energy does not change significantly (within 0.1 eV) with x . From the reflectivity spectra, presented in Fig. 1, we could make several obser-

vations:

- a) The transition energy of the first doublet changes very little with x in the $\text{GaS}_{1-x}\text{Se}_x$ compounds.
- b) The Ga 3d and In 4d structures do not shift significantly in the $\text{Ga}_{1-x}\text{In}_x\text{Se}$ compounds.
- c) All structures depend strongly on the temperature, showing a very small energy shift, but a remarkable sharpening.

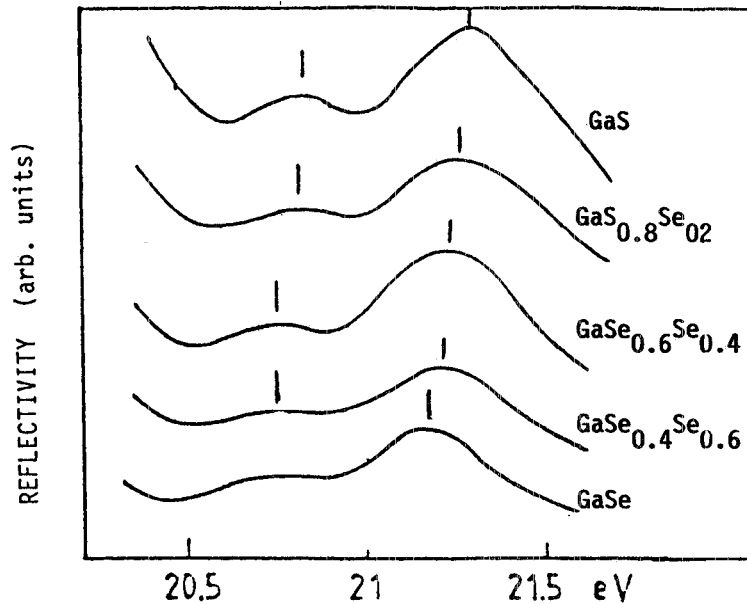


Fig. 1

From the above observations we conclude that the core excitons in the III-VI layered compounds are strongly localized, since they depend very weakly on the local crystal field. The core-exciton phonon coupling is also important in determining the linewidth, and a comparison with the photoemission linewidth of the core level should take into account this effect (unfortunately, the available photoemission set-up does not have enough resolution to allow a study of the phonon broadening of the core level). Finally, in Fig. 2 we compare for all the compounds investigated here several energies. The reference energy is taken at the top of the valence band. The Ga 3d and In 4d binding energies are reported in the lowest part of the figure. Starting from these levels we add the energies of the first reflectivity structures in order to obtain the energies of the final states of the core excitons. It is striking that these energies do not change with the compounds or with the Ga 3d or In 4d initial states. Once more, we have a strong indication of the localized nature of the core excitons. In Fig. 2 we show also the energy of the bottom of the conduction bands, the big shift of which is responsible for the

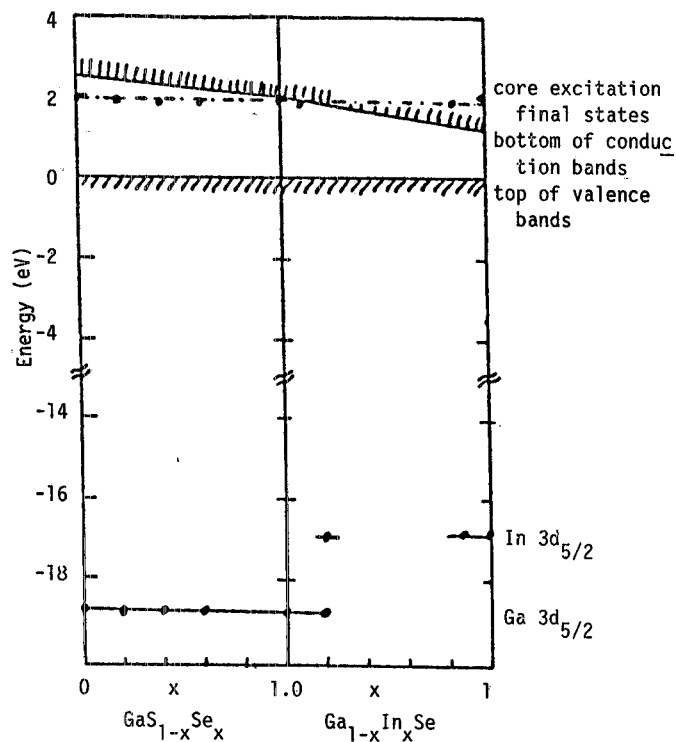


Fig. 2

variation of the binding energy of the core excitons. In particular, the core exciton final states and the bottom of the conduction bands cross each other around $\text{Ga}_{0.1}\text{In}_{0.9}\text{Se}$, indicating that going towards pure InSe the core excitons form resonant states in the continuum of the conduction bands. Thus, it is not clear the meaning of "binding energy" for such localized excitons and any attempt of associating the core excitons with particular minima of the conduction bands becomes meaningless.

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