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Effect of intercalated lithium on the electronic band structure of indium selenide

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The effect of intercalated lithium on the electronic band structure of the β and γ polytypes of InSe has been investigated using a tight-binding method. The energy bands of the pure polytypes were calculated and the results compared with previous work. The tight-binding parameters associated with intercalated lithium atoms were obtained using tabulated atomic functions. The modifications of the energy bands produced by the introduction of one lithium atom per formula unit In_2Se_2 were calculated for the lowest potential-energy position of the lithium atom in the van der Waals gap between layers. The intercalation-induced changes in the smallest and next-to-smallest direct band gaps were determined and compared with experimental data. An interpretation of a photoluminescence peak produced by lithium intercalation is given.

I. INTRODUCTION

The insertion of lithium into layered materials has attracted significant interest as a consequence of the possible use of such materials as electron exchange electrodes in solid-state batteries. Such an application is related to the intercalation capacity and the modifications of the electronic properties of the bulk material. Intercalated InSe (Ref. 1) gives a voltage of 2.6 V against a lithium anode and exhibits a change in conductivity of up to 2 orders of magnitude.[2]

InSe is a layered material consisting of two-dimensional Se-In-In-Se layers between which the binding is weak due to the van der Waals forces. The space between successive layers is known as a van der Waals gap. The stacking of the layers is always compact, but there are four possible stacking arrangements leading to the four polytypes β, ϵ, γ, and δ. Only three of these polytypes (β,ϵ,γ) have been observed for InSe. Bridgeman-grown crystals are generally of the type γ. The difference in total energy between the various polytypes is so small that one practically always finds a high density of stacking faults in a given sample.

Although many of the experimental results that have been obtained are for γ-InSe, no band-structure calculations are available in the literature for this polytype. All existing calculations are for the β and ϵ polytypes which have a simpler first Brillouin zone. The first band-structure calculation for this family of materials was made for GaSe.[3] A calculation for InSe within a tight-binding model has been carried out in a two-dimensional approximation.[4] Extensions to the three-dimensional case have been developed using the pseudopotential method[5] and the tight-binding method.[6,7] Including the spin-orbit interaction in the tight-binding calculation[8] has a non-negligible effect on the InSe band structure. Pseudopotential calculations for ϵ-InSe are also available,[9] but without spin-orbit interaction.

Lithium insertion[10,11] in γ-InSe has been shown to affect both the electronic and optical properties. Possible interstitial sites for Li atoms in γ-InSe have been discussed and their relative energies determined.[12] Lithium diffusion paths[13] in γ-InSe have also been determined by *ab initio* calculations.

The optical properties near the band edges of pure InSe have been investigated and compared with the calculated band structure.[8] Sharp excitonic peaks are observed in the absorption spectrum at low temperature corresponding to the three absorption thresholds. The first threshold at 1.3 eV is related to the direct absorption between the s,p_z valence-band states and s conduction-band states. The second at 2.5 eV is related to transitions from p_x,p_y valence-band states to s conduction-band states, and the third at 2.9 eV is related to transitions from the spin-orbit split-off valence band to the s conduction band. More recent results[14] on pure InSe at 10 K with the electric vector of the radiation perpendicular to the c axis allow one to distinguish the $n=1$ and 2 excitonic transitions as well as the LO phonon replicas to the $n=1$ excitonic state.

The effect of Li insertion on the interband optical absorption peaks is rather weak, but nevertheless, clearly observable. The experimental data for the energies of the excitonic transitions have been analyzed[14] to yield the corresponding energy gaps in the band structure. In Fig. 1 are shown the shifts in energy of the smallest direct band gap E_1 and the next-to-smallest band gap E_2 in γ-InSe as functions of the lithium content.[11] We see that the E_1 gap increases as the Li concentration increases, whereas the E_2 gap decreases.

The excitonic transitions persist after Li insertion, which suggests that all of the Li 2s electrons do not transfer to the conduction band and thus transform the semiconducting InSe into a metal.[15,16] If we had a metallic transition, the Coulomb interaction between the electron and hole of the exciton would be screened and the excitonic state would be washed out. The persistence of the excitonic transitions in highly intercalated InSe suggests that the Li 2s electrons form a low mobility impurity band or are efficiently trapped into localized states.

The photoluminescence spectrum of InSe is

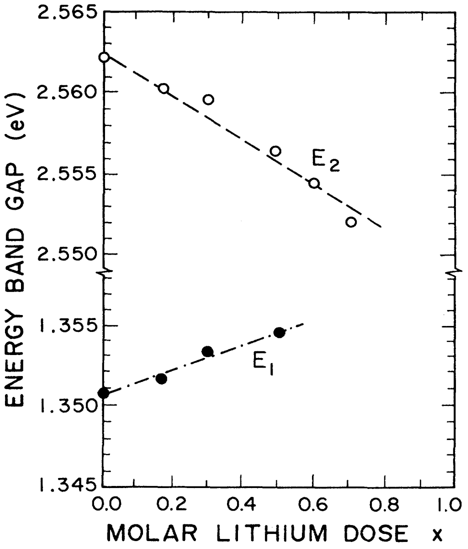

FIG. 1. Energy gap vs lithium content x in Li_xInSe for the smallest and next-to-smallest energy gaps E_1 and E_2 at 5 K.

significantly modified by the intercalation of Li.[10] A new photoluminescence peak appears at a photon energy somewhat less than that of the fundamental photoluminescence peak of pure InSe as shown in Fig. 2. We attribute this new peak to radiation emitted by the decay of an exciton associated with an electron in a Li 2*s* impurity band and a hole at the top of the valence band.

II. THEORETICAL DEVELOPMENT

We have developed a tight-binding scheme for calculating the electronic band structure of both β- and γ-InSe. Our procedure is based on the overlap-reduced semiempirical tight-binding method of Doni *et al.*[7] who considered the case of β-InSe. The Slater-Koster procedure[17] was used to express the overlap and interaction integrals of the tight-binding method in terms of the basic overlap integrals S_{ij} and interaction integrals V_{ij}. Only two-center integrals were considered. The spin-orbit interaction was taken into account as in the work of Piacentini *et al.*[8] The atomic states considered are Se 4*s* and 4*p* and In 5*s* and 5*p* whose energies were taken from Doni *et al.*

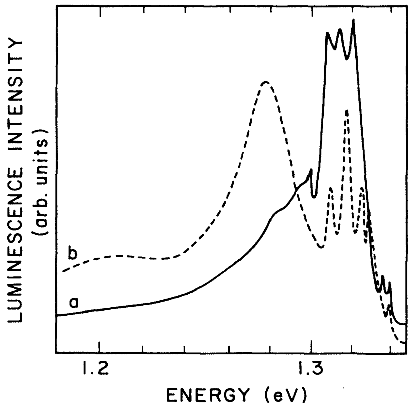

FIG. 2. Photoluminescence spectra for γ-InSe before (a) and after (b) lithium intercalation at 5 K under 1.916 eV excitation by a Kr^+ laser.

The structure of γ-InSe is simpler than that of β-InSe, because the former has only four atoms per unit cell, whereas the latter has eight atoms. The difference in structure arises from the difference in stacking of successive layers; the interatomic distances within a layer are essentially the same in both polytypes. In view of these similarities, we have taken the basic overlap and interaction parameters for γ-InSe to be the same as those given by Doni *et al.* with the following exceptions. In order to reproduce the experimental values of the smallest band gap E_1 and the next-to-smallest band gap E_2, the interlayer parameters $S_{\text{Se-Se}}(pp\sigma)$ and $\bar{V}_{\text{Se-Se}}(pp\sigma)$ together with the crystal field parameters $K(\text{In } 5s)$, and $K(\text{Se } p_x)$, $K(\text{Se } p_y)$, and $K(\text{Se } p_z)$ were varied. The values thus obtained are tabulated in Table I. Furthermore, the overlap and interaction parameters S and $\bar{V}$ of Doni *et al.* for the In-In interactions were multiplied by 1.011.

For β-InSe we used the same values of the parameters S_{ij} and $\bar{V}_{ij}$ that were used for γ-InSe for the nearest-neighbor intralayer In-In, In-Se, and Se-Se interactions both parallel and perpendicular to the *c* axis. The crystal-field parameters were also taken to be the same as for γ-InSe. The interlayer Se-Se parameters were scaled from the values for γ-InSe by the ratio of the inverse squares of the Se-Se separations in the two polytypes.

Having established the tight-binding scheme for the pure β- and γ-polytypes of InSe, we then proceeded to generalize the scheme to include the presence of intercalated Li atoms. We assume that the Li atoms occupy the sites of lowest potential energy[13] in the Van der Waals gap between layers. Since intercalation of lithium leads to only a small increase in the interlayer spacing, we have neglected any change in the intralayer tight-binding parameters of InSe. The Se-Se interlayer parameters were modified as indicated in Table I. The overlap and interaction parameters for the interaction of a Li atom with the nearest Se and In atoms were estimated using the tabulated atomic functions of Clementi and Roetti.[18] The electronic band structure of the intercalated InSe was then obtained by diagonalizing the Hamiltonian matrix. The changes in the E_1 and E_2 gaps thus obtained turned out to be too large. The parameters involving Li were then varied until agreement was achieved between the theoretical and experimental values of the E_1 and E_2

TABLE I. Values of the tight-binding parameters for γ-InSe. The notation is that of Ref. 7. $\bar{V}$ and K are in rydbergs.

	Se-Se interlayer parameters		Crystal-field parameters	
	without Li	with Li		
$S(pp\sigma)$	−0.010	−0.0087	$K(\text{Se } 4p_x)$	0.0203
			$K(\text{Se } 4p_y)$	0.0203
$\bar{V}(pp\sigma)$	0.002	0.002	$K(\text{Se } 4p_z)$	0.1150
			$K(\text{In } 5s)$	−0.0433

TABLE II. Values of the tight-binding parameters for lithium-intercalated γ-InSe. $\bar{V}$ and K are in rydbergs.

	S	$\bar{V}$	K
Li-Se ($ss\sigma$)	0.026 36	−0.000 318	
Li-Se ($sp\sigma$)	−0.007 7	0.002 7	
Li-In ($ss\sigma$)	0.004 143	−0.000 313	
Li-In ($sp\sigma$)	−0.046 65	0.000 669	
Li (2s)			−0.063

gaps and the position of the lithium-induced photoluminescence peak. The resulting values for the Li parameters are listed in Table II.

III. NUMERICAL RESULTS

The electronic band structure of pure γ-InSe which we have obtained is shown in Fig. 3 for the high-symmetry directions in the first Brillouin zone. The notation for the high-symmetry points is that of Slater.[19] The smallest direct gap (E_1) occurs at Γ between the s,p_z valence band and the s conduction band. The next larger direct gap (E_2) occurs at Γ between the p_x,p_y valence band and the s conduction band. The indirect gaps are not smaller than the direct gap E_1.

For the case of pure β-InSe, we plot our results for the band structure in Fig. 4 for several high-symmetry directions in the first Brillouin zone. These results are very similar to those of Doni *et al.* In particular, both sets of results give an indirect gap between Γ and M that is somewhat smaller than the direct gap E_1 at Γ.

In Fig. 5 we present the band structure for lithium-intercalated γ-InSe with the composition $\mathrm{Li}_{0.5}\mathrm{InSe}$ and the Li atoms occupying the $A_{3\text{-}2}$ sites[13] in the Van der Waals gap between layers. The band associated with the Li 2s state is seen to lie just below the conduction-band edge and is separated from the latter by 0.036 eV at Γ. The effect of the intercalated lithium on the InSe bands is too small to be observable on the scale of the figure. However, the effects on the E_1 and E_2 gaps are revealed by the numerical results given in Table III.

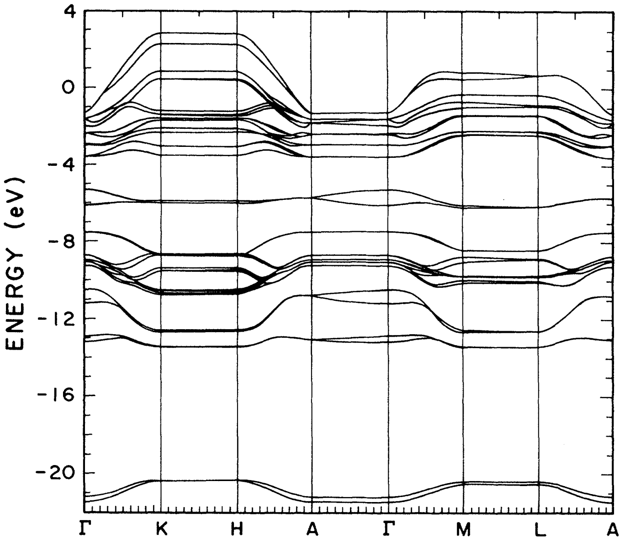

FIG. 4. Energy bands for pure β-InSe.

The occurrence of the Li 2s band in the fundamental gap of InSe provides a natural explanation for the new photoluminescence peak produced by Li insertion. Excitation with photons having energy greater than the band gap creates electron-hole pairs. An electron in the Li 2s band can then recombine with a hole accompanied by the emission of a photon whose energy is equal to the difference between the valence-band edge and the lower edge of the Li 2s band. The semiconducting properties of lithium-intercalated γ-InSe are consistent with the Li 2s

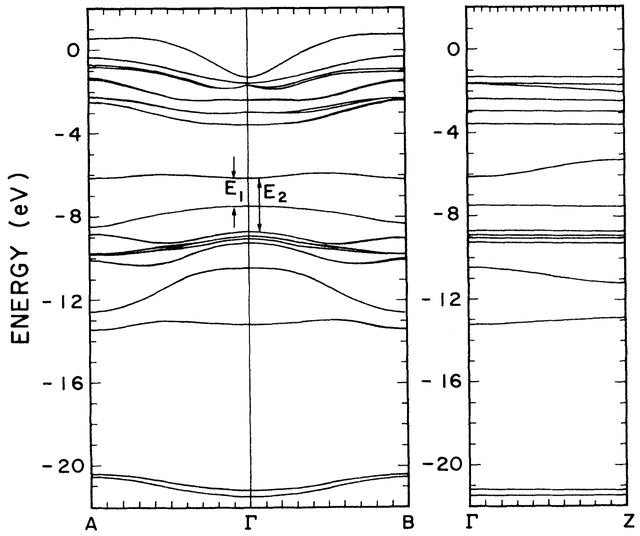

FIG. 3. Energy bands for pure γ-InSe.

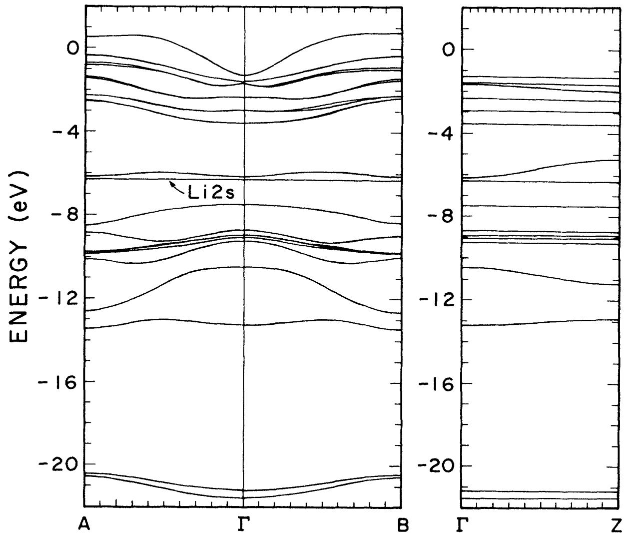

FIG. 5. Energy bands for lithium-intercalated γ-InSe with the composition $\mathrm{Li}_{0.5}\mathrm{InSe}$. The gap between the Li 2s band and the conduction band just above it is 0.036 eV at Γ, but is exaggerated for clarity.

TABLE III. Values of the E_1 and E_2 energy gaps with and without lithium intercalation in γ-InSe.

	Pure γ-InSe	$\mathrm{Li_{0.5}InSe}$
E_1	1.3507 eV	1.3546 eV
E_2	2.5622	2.5565

band lying within the valence-conduction band gap.

The band structure for lithium-intercalated β-InSe with the composition $\mathrm{Li_{0.5}InSe}$ and the Li atoms occupying the octahedral sites in the van der Waals gap between layers is shown in Fig. 6. For the composition considered, there are two Li atoms per unit cell and the two corresponding Li $2s$ bands can be split by their interaction via the Se and In atoms between the Li atoms. As in the case of γ-InSe, the Li $2s$ bands lie just below the conduction-band edge and are separated from the latter by 0.057 and 0.066 eV at Γ.

IV. CONCLUSIONS

A tight-binding scheme has been developed for pure β-InSe and γ-InSe using the overlap-reduced semiempirical method. The procedure satisfactorily accounts for the direct energy gaps of the two polytypes. The tight-binding scheme has been generalized to include the effect of intercalated lithium atoms. The shifts in the direct gaps and the appearance of a new peak in the photoluminescence spectrum observed experimentally for lithium-intercalated γ-InSe are consistent with the calculated electronic structure. The presence of lithium leads to an impurity band in the energy gap between the conduction and valence bands.

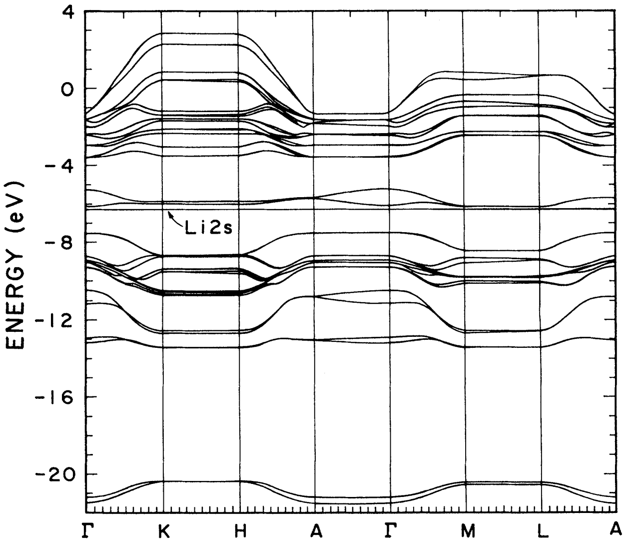

FIG. 6. Energy bands for lithium-intercalated β-InSe with the composition $\mathrm{Li_{0.5}InSe}$. The gaps between the Li $2s$ bands and the conduction band just above it are 0.057 and 0.066 eV at Γ, but are exaggerated for clarity.

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