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REPORT SUMMARY

The purpose of the project on Superionics supported by DARPA Contract No. N00014-88-K-0392 is to develop a physical understanding of the elements of a solid state battery consisting of a lithium anode, a lithium-doped borate glass separator and a lithium-intercalated InSe cathode. In this report a theoretical analysis based on a tight-binding model is presented for the electronic structure of both pure and lithium-intercalated InSe. An understanding of the electronic structure is necessary for an understanding of the electrical conductivity due to both electronic motion and lithium-ion motion. The conductivity is an important parameter for the performance of the solid state battery.

For an appropriate choice of the tight-binding parameters the calculated variation of the smallest and next-to-smallest direct band gaps with lithium content agrees well with experimental data. A lithium impurity band appears in the forbidden gap between the valence and conduction bands. The presence of this impurity band provides a natural explanation for a photoluminescence peak that appears in the lithium-intercalated material.

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Effect of Intercalated Lithium on the Electronic Band
Structure of Indium Selenide

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Abstract

The effect of intercalated lithium on the electronic band structure of the ρ - 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 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.

1. 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⁽¹⁾ gives a voltage of 2.6V against a lithium anode and exhibits a change in conductivity of up to two 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⁾ Including the spin-orbit interaction in the tight-binding calculation⁽⁷⁾ has a non-negligible effect on the InSe band structure. Pseudopotential calculations for ϵ -InSe are also available,⁽⁸⁾ but without spin-orbit interaction.

Lithium insertion^(9,10) 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.⁽¹¹⁾ Lithium diffusion paths⁽¹²⁾ 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.⁽⁷⁾ 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⁽¹³⁾ on pure InSe at 10K with the electric vector of the radiation perpendicular to the c -axis allow one to distinguish the $n=1$ and $n=2$ excitonic transitions as well as the LO phonon replicas of the $n=1$ excitonic state.

The effect of Li insertion on the interband optical absorption peaks is rather weak, but nevertheless, clearly observable. In Fig. 1 are shown the shifts in frequency of the smallest direct band gap E_1 and the next-to-smallest band gap E_2 as functions of the lithium content.⁽¹⁰⁾ We see that the E_1 gap increases in frequency as the Li concentration increases, whereas the E_2 gap decreases in frequency.

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.^(14,15) 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 significantly modified by the intercalation of Li. A new photoluminescence peak appears at a photon energy somewhat less than that of the fundamental exciton peak of pure InSe as shown in Fig. 2. This new peak may be associated with the Li-2s band lying in the fundamental gap of InSe.

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 semi-empirical tight-binding method of Doni et al.⁽¹⁶⁾ 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.⁽⁷⁾ The atomic states considered are Se 4s and 4p and In 5s and 5p whose energies were taken from Doni et al.

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. The interlayer parameters $S_{\text{Se-Se}}(\text{pp}\sigma)$ and $\bar{V}_{\text{Se-Se}}(\text{pp}\sigma)$ together with the crystal field parameters $K(\text{In } 5s)$, $K(\text{Se } p_x)$, $K(\text{Se } p_y)$, and $K(\text{Se } p_z)$ were varied in order to reproduce the experimental values of the smallest band gap E_1 and the next-to-smallest band gap E_2 . The values thus obtained are tabulated in Table I. Interactions beyond those tabulated by Doni et al. were included by scaling the corresponding Doni parameters with a factor d^{-2} , where d is the interatomic distance of the interacting atoms. The interactions were cut off at $d=8.77\text{\AA}$. Furthermore, the overlap reduction parameters α_R and α_M of Doni et al. were multiplied by 1.008 to produce the best fit to the experimental data.

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⁽¹²⁾ 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 calculated 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 Li parameters were then varied until agreement was achieved between the theoretical and experimental gaps. The resultant values for the Li parameters are listed in Table II.

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 no 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 $\text{Li}_{0.5}\text{InSe}$ and the Li atoms occupying the A_{3-2} sites⁽¹²⁾ 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. 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. There is excellent agreement between the theoretical values and the experimental values shown in Fig. 1.

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 band lying within the valence-conduction band gap.

The band structure for lithium-intercalated β -InSe with the composition $\text{Li}_{0.5}\text{InSe}$ and the Li atoms occupying the octahedral sites in the Van der Waals gap between layers is shown in Fig. 6. As in the case of γ -InSe, the Li-2s band lies within the gap between the valence and conduction bands. There is a small splitting of the Li-2s level in the vicinity of the M-point. 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.

Conclusions

A tight-binding scheme has been developed for pure β -InSe and γ -InSe using the overlap-reduced semi-empirical 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.

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Figure Captions

Fig. 1. Energy gap versus lithium content in γ -InSe for the smallest and next-to-smallest energy gaps E_1 and E_2 .

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

Fig. 3. Energy bands for pure γ -InSe.

Fig. 4. Energy bands for pure β -InSe.

Fig. 5. Energy bands for lithium-intercalated γ -InSe with the composition $\text{Li}_{0.5}\text{InSe}$.

Fig. 6. Energy bands for lithium-intercalated β -InSe with the composition $\text{Li}_{0.5}\text{InSe}$.

TABLE I. Values of the tight-binding parameters for γ -InSe. The notation is that of Ref. 16. $\bar{V}$ 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 ($ss\sigma$)	0.02636	-0.000318	
Li-Se ($sp\sigma$)	-0.0077	0.0027	
Li-In ($ss\sigma$)	0.004143	-0.000313	
Li-In ($sp\sigma$)	-0.04665	0.000669	
Li (2s)			-0.066

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

	pure γ -InSe	lithium-intercalated γ -InSe
E_1	1.3335 eV	1.3368 eV
E_2	2.5451	2.539

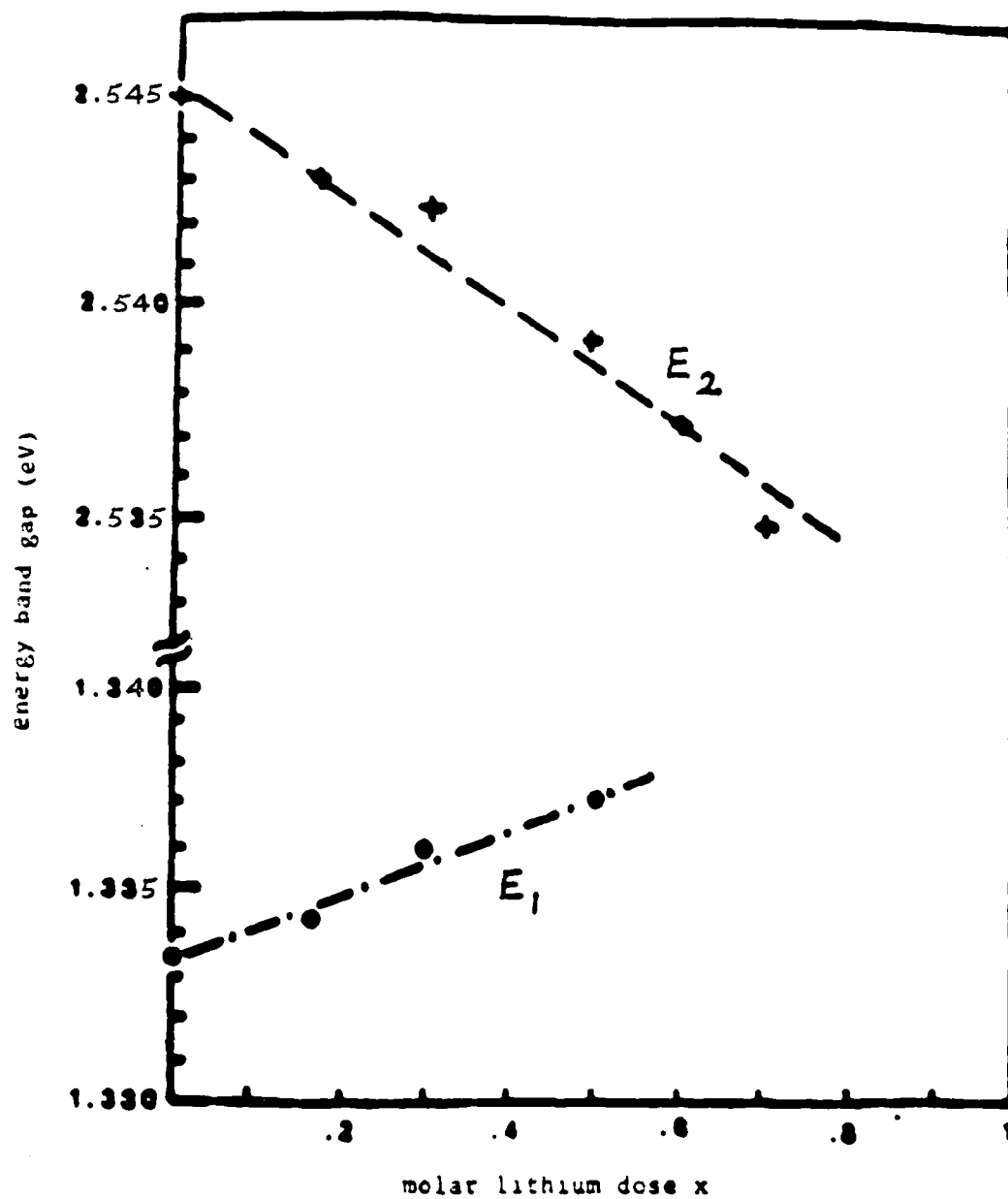


Fig. 1

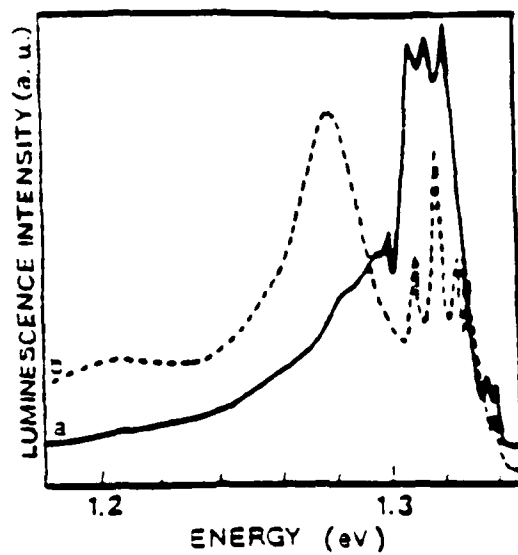


Fig. 2

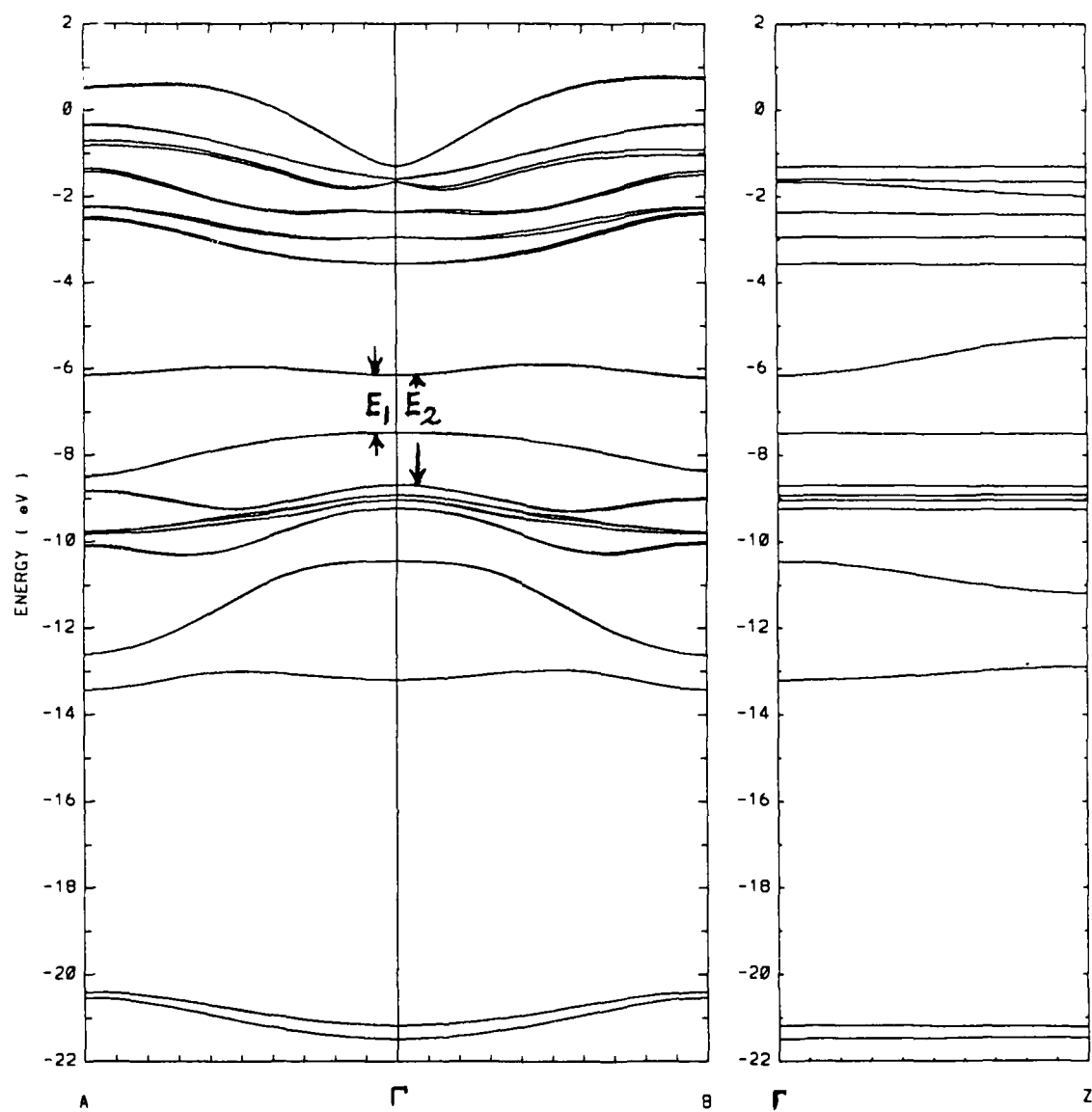


Fig. 3

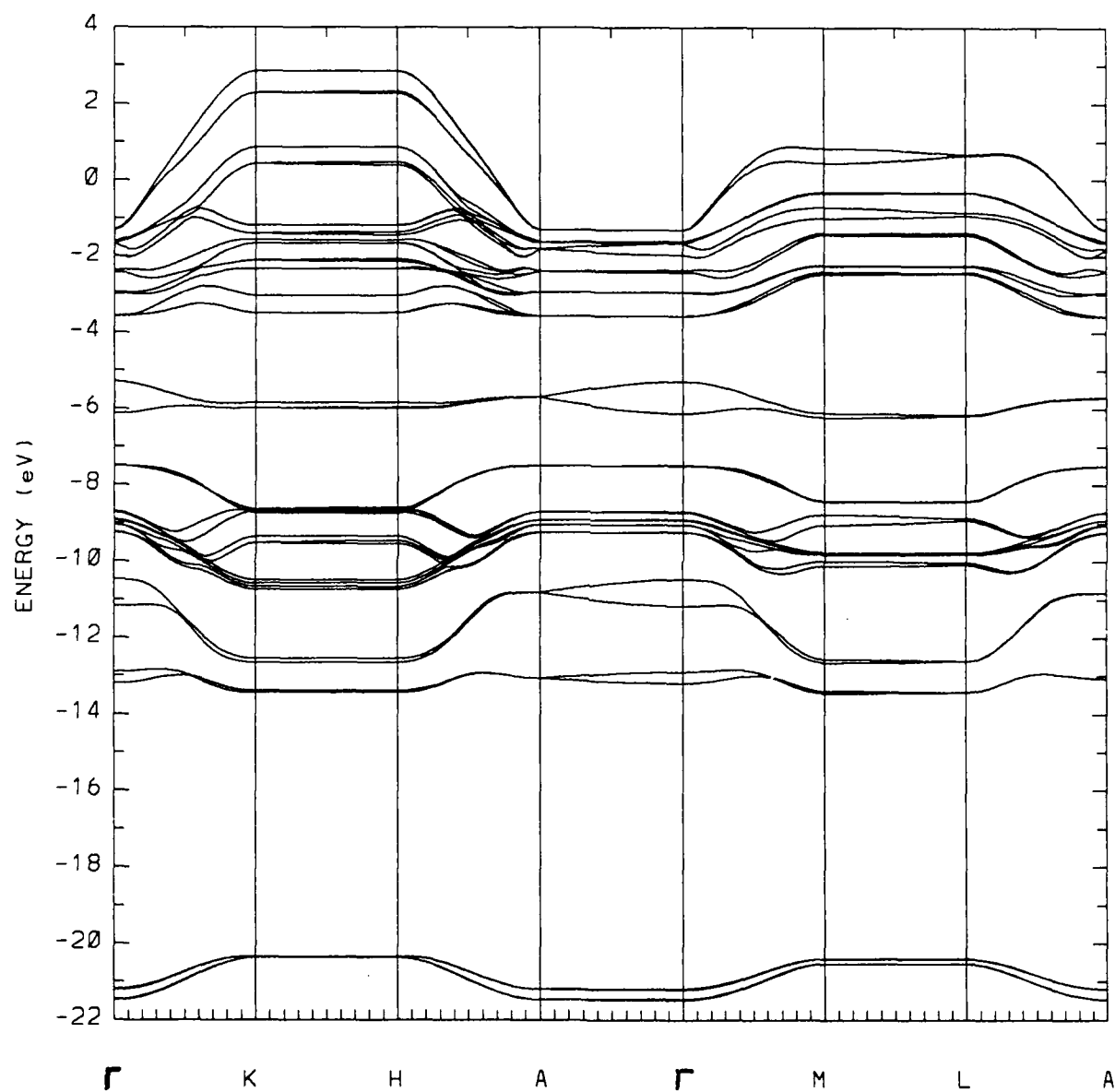


Fig. 4

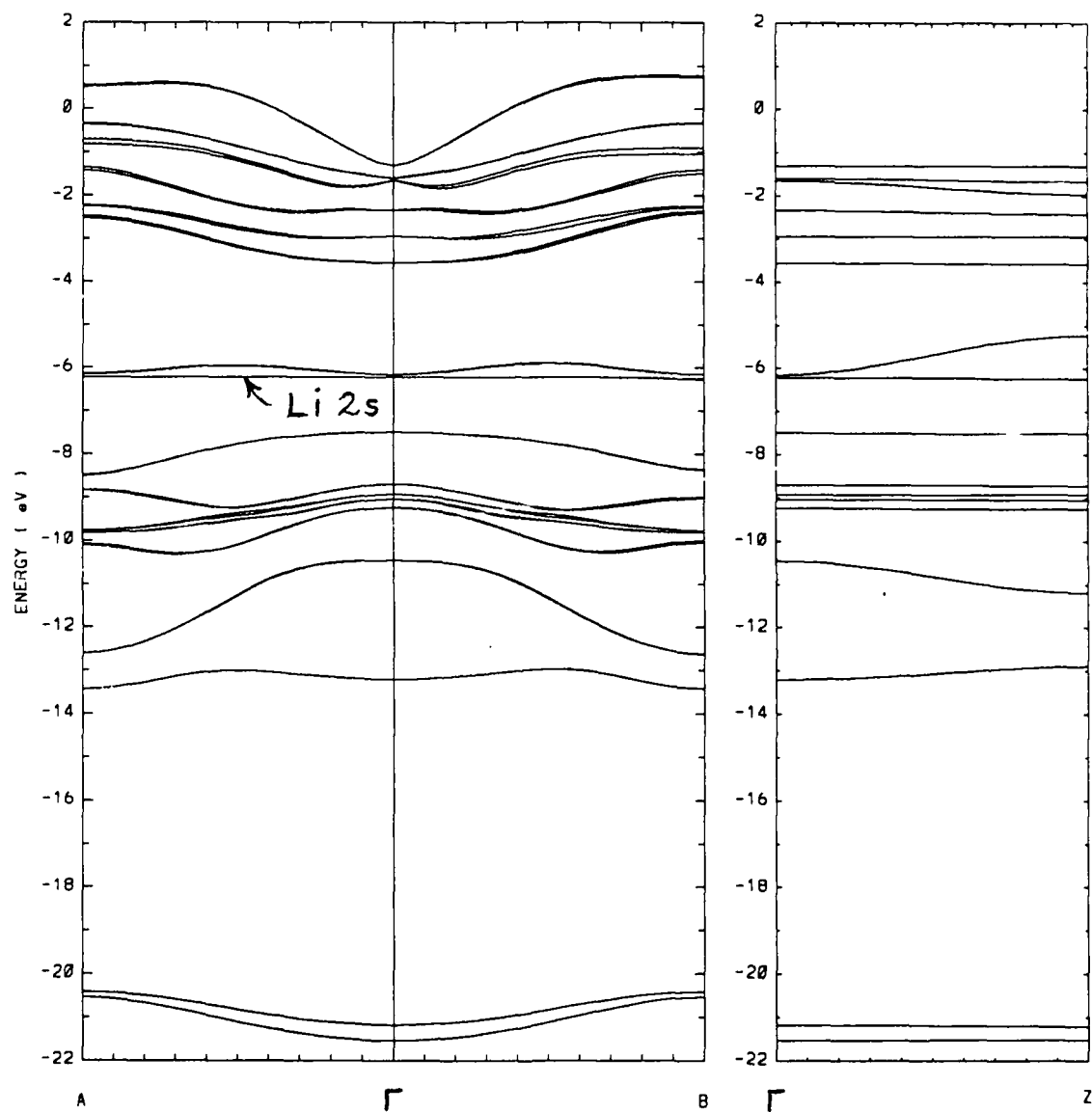


Fig. 5

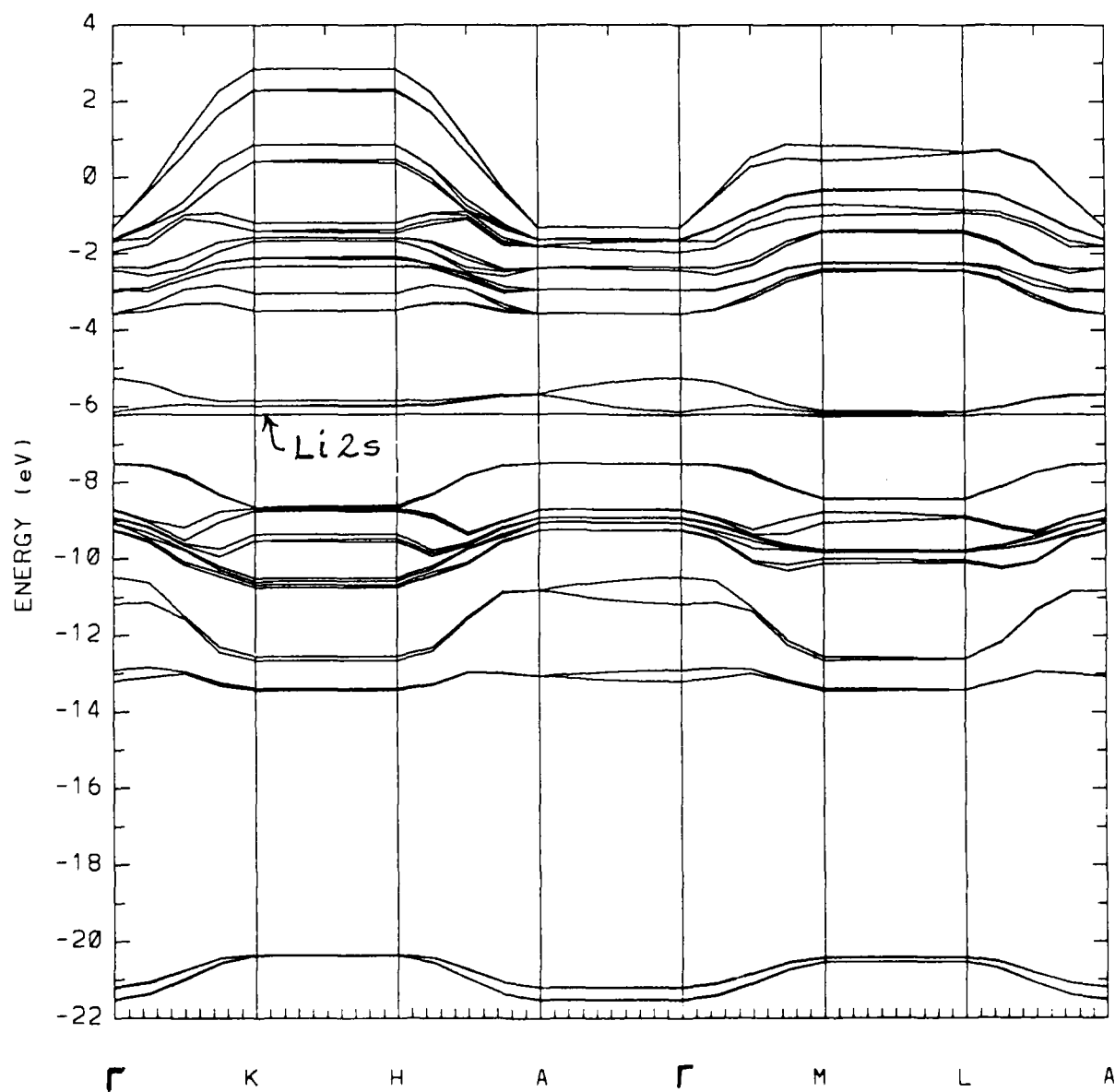


Fig. 6