

ELECTRON AND PHONON ASPECTS IN A LITHIUM INTERCALATED InSe CATHODE

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Summary

Lithium intercalated InSe has been shown to function as a cathode in lithium batteries. Lithium insertion in InSe results in structural modification to create a superlattice that induces new Raman peaks by folding of the phonon branches. The presence of alternating sheets of Li^+ ions causes alterations in the electronic band structure due to complementary Coulomb interaction that is itself evident through changes in exciton binding energies. In the presence of Li^+ ions, new radiative recombination centres are also observed.

Introduction

Layered materials, such as the III - VI compounds, have been shown to function as cathodes in lithium batteries. InSe has been demonstrated [1] to yield reasonable cathode characteristics when used in a lithium cell with lithium perchlorate as the electrolyte and discharged with a current density up to 0.7 mA cm^{-2} at 25°C .

The intercalated substance, LiInSe , is, in general, a mixed electronic and ionic conductor. The performances of a lithium battery using intercalation cathodes will depend on the intercalation capacity of the cathode material which is, in turn, related to its electronic structure.

Insertion of Li into a layered compound, such as InSe, produces structural changes that are observable through the lattice dynamics and the electronic band structure modifications of the host. The structural changes originate from the insertion of atoms into the van der Waals gap of the host compound, and consequently, from the formation of a new structure with a superlattice that has an elementary unit-cell which is larger than that of the pure InSe. This new superlattice leads to the folding of the phonon branches where non-zone centre modes of the host structure will appear at the centre off the Brillouin zone. The modes therefore become Raman active and are observable by means of light scattering spectroscopy.

Intercalation also influences the electronic band structure of the host. The 1s electron binding energy of the lithium atom, when intercalated in

InSe, is very small compared with the band gap of the host material. Therefore, all the lithium atoms are ionized and contribute free electrons to the conduction band. Alternating layers of Li^+ ions give rise to an additional Coulomb interaction and thereby modify the band structure of the material. Such modifications are reflected in the excitonic structure and can be observed in investigating the optical transitions. We report here a comparison between the radiative spectra of pure and lithium-intercalated InSe. From this comparison, an increase in anisotropy is found upon intercalation and this suggests a more pronounced two-dimensionality. New recombination bands are also observed and the temperature dependence of their energy position significantly differs from that observed in the pure material. These bands can therefore be related to radiative recombination involving lithium donor centers.

Electronic band structure of InSe

Indium selenide is a layered semi-conductor of the III - VI family, and consists of stacked hexagonal layers each comprising four, close-packed, monoatomic sheets in the sequence Se-In-In-Se. The interlayer bonds are weaker than those inside a single layer and this facilitates the existence of several polytypes corresponding to different stacking sequences of the layers. The simplest and most frequently described polytypes in the III - VI family are β , ϵ and γ . The ϵ and β phases are 2H hexagonal polytypes, while the γ modification has a 3R rhombohedral structure. Due to the particular binding between the sandwiches, real van der Waals gaps appear in the structure between two successive chalcogenide layers. These gaps, empty in pure and perfect materials, can be thought of as channels through which intercalation guest atoms or molecules can diffuse without significantly altering the host structure.

The electronic band structure of InSe is almost flat in all directions within the layer plane. The absorption spectra reveal absorption edges preceded by excitonic peaks that correspond to transitions from successive valence bands to the conduction band [2, 3]. The first absorption edge at 1.3525 eV represents the direct transitions from the top valence band (Γ_4^-) to the lowest conduction band (Γ_3^+) at the centre of the Brillouin zone. A secondary minimum of the conduction band, at the K point of the Brillouin zone, is situated only 50 meV below the position at the Γ point. The second absorption edge at 2.53 eV corresponds to transitions from the lower valence band (Γ_9^-) to the conduction band (Γ_3^+).

Experimental

The InSe crystals were grown by the Bridgman method from a non-stoichiometric melt and consisted mainly of γ -polytype [4]. The samples

studied were n-type with a native donor level showing an ionization energy of 18.5 meV and a free-carrier concentration of $10^{14} - 10^{15} \text{ cm}^{-3}$. Lithium intercalation was performed by direct reaction with *n*-butyllithium dissolved in hexane forming a 1.6 M solution.

Experiments were carried out in a controlled atmosphere and electrical measurements were performed during intercalation. Optical measurements were undertaken with a delay of more than four weeks after the intercalation. The samples were mounted in a variable temperature cryostat operating in the range 5 - 300 K. The photoluminescence was excited by a Kr (647.1 nm) or an Ar (457.9 nm) laser with excitation densities of $10^{19} \text{ photons cm}^{-2} \text{ s}^{-1}$. The emitted light was dispersed by a 600 mm monochromator and fed to an ITT FW 118 cooled photomultiplier. The Raman scattering spectra were measured by means of the photon counting method with a 600 mm double holographic grating monochromator and an ITT FW 130 cooled photomultiplier. The 488 nm line of an Ar-ion laser was used as the light source.

Results

Figure 1(a) shows the light scattering spectra observed at 5 K in the region of the first-order scattering of polar optical modes. The spectra obtained from lithium-intercalated samples are given in Fig. 1(b). Two new features appear in the spectra of the intercalated samples: (i) the scattering intensity ratio of the Γ_3^1 -LO mode (three dimensional character) to the Γ_1^1 -LO mode (two-dimensional character) is enhanced; (ii) new bands, weak in intensity, appear in the vicinity of the main peaks: at 132 cm^{-1} near the Γ_2^1 mode (118 cm^{-1}) and at 190 cm^{-1} near the Γ_3^1 -TO mode (182 cm^{-1}). The latter new peaks may arise from a folding of the Brillouin zone to create a new superlattice due to the intercalation of lithium in the van der Waals gaps of InSe. The elementary unit cell of the superlattice is larger than that of the pure InSe. The new peak at 190 cm^{-1} coincides well with the Γ_1^1 -TO mode which is calculated at 186 cm^{-1} when using a force constant determined from the observed frequencies of the Γ_1^2 and Γ_3^1 modes at room temperature [5].

Figure 2 represents the emission spectra of pure and lithium-intercalated InSe. A significant difference is again observed between the two spectra. The photoluminescence spectrum of pure InSe taken at 5 K consists of a series of emission bands that can be grouped into two sets. The first set is at a high energy (near the "second gap") in the vicinity of 2.56 eV. The emission band observed in this region is situated at 2.545 eV and can be attributed to the radiative recombination of free excitons [6]. The second set of emission bands is found at energies below the direct absorption at 1.3525 eV. The highest in energy is a narrow line at 1.338 eV which is close to the absorption band for free excitons at 1.336 eV [7] related to the direct gap. Below this band, two emission lines are present at 1.334 eV

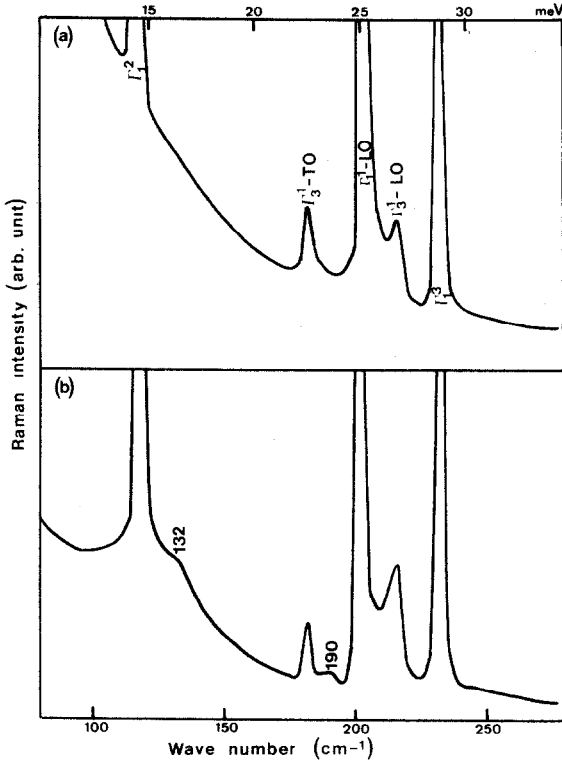


Fig. 1. Raman intensity vs. wavenumber of (a) pure InSe and (b) Li-intercalated InSe taken at 5 K.

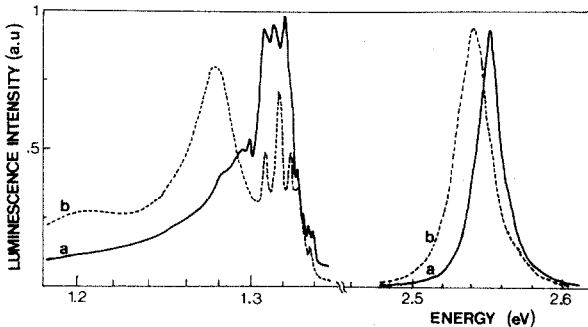


Fig. 2. Luminescence intensity at 5 K of different recombination bands of (a) pure InSe and (b) Li intercalated InSe.

and 1.331 eV. Time-resolved photoluminescence studies strongly suggest that these satellite lines are caused by the radiative recombination of bound excitons [8].

At lower energies, the strong emission band is resolved into three peaks at 1.322 eV, 1.317 eV and 1.311 eV. The assignment of these peaks is still

a matter of controversy. Brebner *et al.* [8] have attributed this band to recombination through donor-acceptor pairs. This assignment is substantiated by an evolution with time of the band which gradually shifts to lower energies. Other authors associate this band with an electron-hole liquid [9]. Weaker bands at lower energies are equated with structural defects.

After intercalation, the photoluminescence spectrum is drastically modified (Fig. 2(b)). The variation of the 2.545 eV luminescence peak as a function of the intercalation dose is displayed in Fig. 3. The "second gap" peak at 2.545 eV shifts towards a lower energy with increase in the degree of lithium intercalation.

Analogous behaviour is observed near the first direct gap. The exciton peaks move towards higher energy. The donor-acceptor pair recombination bands are better resolved and are shifted to higher energies. Two new bands appear upon lithium intercalation, at 1.2815 eV and 1.198 eV. Figure 4 shows the energy variation of the more intense band as a function of temperature. The position of this band first moves towards higher values with increasing temperature, and then decreases. Figure 5 represents the temperature dependence of the energy position of the second, and weaker, band situated at 1.198 eV at 5 K. The position of this peak steadily shifts towards

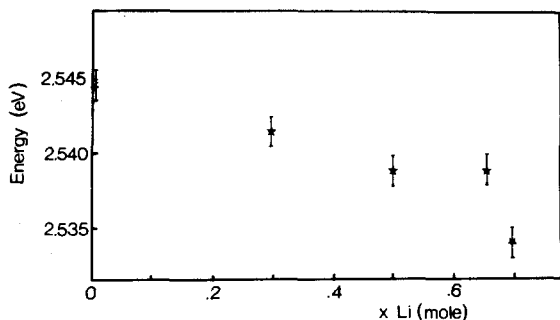


Fig. 3. Energy shift of the free exciton recombination band related to the lower valence band as a function of Li dose into InSe.

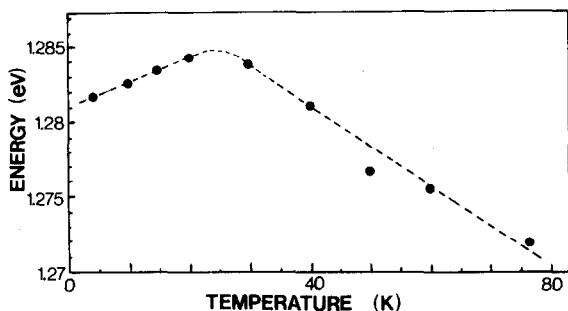


Fig. 4. Energy position *vs.* temperature of the luminescence peak appearing after Li insertion.

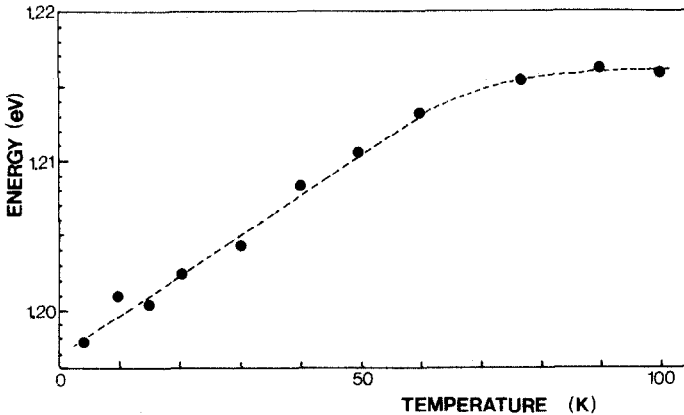


Fig. 5. Energy position of the lower luminescence peak associated with Li insertion.

higher energies with increasing temperature. Both these bands are presumably related to optical transitions involving lithium donor centres.

Discussion and conclusions

Lithium intercalation in InSe creates a new periodic layer structure that is different from that of the host compound. This structure corresponds to a new superlattice that can be identified both by the lattice dynamics and by the electronic structure of the system. We have used light scattering to investigate the structural modifications caused by the intercalation, and photoluminescence to study the modifications in the electronic characteristics of the intercalated system.

We shall first discuss the results obtained by light scattering. Because of the small wave vector of light relative to the Brillouin zone dimensions in solids, first-order scattering is confined to the excitation of phonon modes close to the zone center. Non-zone-center modes of the host structure are folded into zone center modes in the intercalation compound, thus resulting in a superlattice structure and in the excitation of additional Raman active modes. Graphite intercalation compounds allow the generation of large varieties of superlattices [10].

The light scattering spectra shown in Fig. 1 are indicative of superlattice formation. The weak peak observed at 132 cm^{-1} results from the folding of the phonon branch, Γ_1^2 , at 118 cm^{-1} of pure InSe, due to the effect of intercalation. The same holds for the new peak at 190 cm^{-1} which is the folded branch, Γ_3^1 of the TO normal mode of the host InSe starting at 182 cm^{-1} at the center of the Brillouin zone.

The fact that the frequencies of the host normal modes are not modified by the intercalation indicates that the intra-layer binding is strong compared with the inter-layer binding and remains practically unperturbed by the intercalation. This suggests that the intercalated layers are not bound

to the host, but that their effect is to change only the symmetry properties of the system to give a new superlattice and zone folding. Therefore, intercalation should not be expected to cause significant changes in the lattice parameters. In addition, the intercalation should be easily reversible.

The effect of intercalation on the electronic structure of the system has been investigated by means of radiative recombination. The results reported here have the same significance as those obtained from studies of the lattice dynamics. Intercalated lithium forms a layer in the van der Waals gap which only weakly influences the intra-layer binding of the host. As shown in Fig. 3, increase in the intercalation induces a shift of the exciton peak towards a lower energy and also causes it to broaden. An opposite effect is observed on the first direct-gap free exciton where the exciton line is shifted by 3 meV towards higher energy after intercalation. The recombination of the donor-acceptor pairs is shifted towards higher energy and the bands are sharpened.

Intercalation of lithium also introduces new luminescence centres at 1.2815 eV and 1.198 eV. Further investigations are required in order to obtain more detailed information on the electronic configuration related to the structural position of the atoms that give rise to these luminescence centres.

The observed characteristics of lithium intercalation in InSe indicate that the lithium is confined to the inter-layer space and that interaction with the host layers is weak. This weak interaction confirms the proposal that lithium-intercalated InSe is a potentially good cathode material for lithium batteries. The finding also suggests that fully reversible intercalation may occur without any mechanical damage to the host.

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