Z. Phys. B – Condensed Matter 76, 451–455 (1989)

Zeitschrift für Physik B Condensed Matter

Theoretical calculations and Raman spectrum of intercalation modes in Li_xInSe

P.A. Burret, M. Jouanne, and C. Julien
Laboratoire de Physique des Solides de l'Université Pierre et Marie Curie,
associé au CNRS, Paris, France

Received April 5, 1989

By using an extended linear-chain model which includes the interlayer forces, we have calculated the new vibrational modes of Li intercalated InSe. The dispersion curves along the $\mathbf{k}_z$ wavevector perpendicular to the layers for the γ-polytype are determined in the first Brillouin zone. Assuming that the interlayer interaction is not modified upon intercalation and the interaction between lithium atom and adjacent layers in the van der Waals plane has the same value than the interlayer one, the new modes are determined with the force constant given by the rigid layer mode of the ε-polytype at 18 cm^{-1}. This model gives the variation of the acoustic branches and the appearance of two optical intercalation modes at higher frequencies. The Brillouin zone boundary modes of the acoustic branches at 18 and 41 cm^{-1} in the pure material are calculated to be 22 and 50 cm^{-1} respectively for $x=1/2$. The dispersion of the new optical branches is flat along the z-direction and frequencies are obtained at 96 cm^{-1} for the Li mode perpendicular to $\mathbf{k}_z$ and at 218 cm^{-1} for the Li mode parallel to $\mathbf{k}_z$. We compare also our results with the Li mode frequencies obtained in a total energy calculation. Raman scattering experiments have been performed in intercalated sample in order to verify the proposed model.

1. Introduction

The properties of intercalation compounds are the subject of increasing importance [1]; their utility in electrochemical systems and in battery applications in particular, is widespread.

Indium selenide has attracted significant interest as an insertion compound because of its capacity, like other layered materials, to insert in its van der Waals plane different foreign species. Studies of pure and inserted monocrystals have been developed using optical spectroscopy based on the particular band structure of the InSe [2], and the presence of plasmon-phonon coupling mode in the inserted sample [3, 4].

In recent papers, interstitial site energies and frequency modes of lithium atoms into γ-InSe have been calculated on ab-initio determination of total energy (DTE) and density functional theory [5, 6]. By probing different portions in the elementary unit cell, three sites between the layer are favourable for insertion operation, two of them are tetrahedral sites (TS) near selenium planes, and one is an octahedral site (OS) in the middle of the van der Waals space (Fig. 1). The frequency of the Li vibration in the layer plane is attempted at about 97 cm^{-1} for all sites [5, 6] and

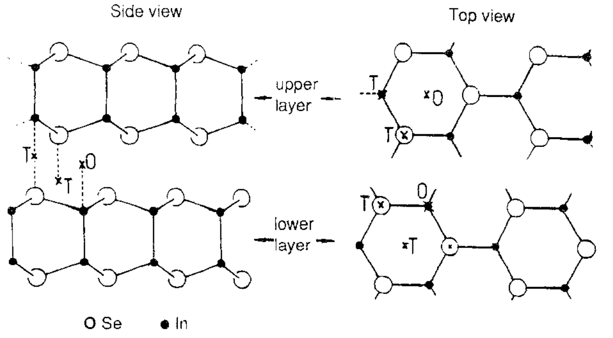

Fig. 1. Perspective view of two layers of γ-InSe with the Li sites in the van der Waals space. Black dots denote In, open circles the Se atoms

along the z-axis perpendicular to the layers is attempted at about 230 cm^{-1} in the OS and at 430 cm^{-1} in the TS [7].

The two-dimensional structure of a layered sample allows to calculate phonon frequencies in the Brillouin zone centre and also their dispersion curves along $\mathbf{k}_z$ in a extended linear chain model (ELCM).

In this paper, we present a theoretical valuation of the vibrational mode frequencies in $\mathrm{Li}_x\mathrm{InSe}$ using a ELCM. Raman scattering spectrum of Li intercalated InSe shows new unknown peaks, and we discuss the attribution of them as vibrations of Li guest atoms in interstitial sites of the van der Waals space.

2. Extented linear chain model (ELCM)

The linear chain model developed by Wieting [8] can be extended to a two-dimensional crystal if the following two important conditions are respected: (*i*) the identical atoms of each elementary cell must be arranged on parallel planes, and each of these planes must contain only one type of atom, (*ii*) the vibration direction must be parallel or perpendicular to these planes. InSe respects these two conditions.

In a simple case, we assume that the inserted Li atom is found in the middle of the van der Waals space and that there is almost one Li per primitive unit cell for $0 \leqq x \leqq 0.5$. Figure 2 shows the linear chain model in this case. In this schematic representation m_1 is the mass of each host layer and $2xm_2$ is the mass of intercalant plane. We assume also that interactions between adjacent layers are not modified by the inserted atoms. Consequently, we consider only two force constants, one interlayer K and one lithium-layer K' as in the Sekine's calculation [9].

The motion equations of the InSe layer (u_n) and of the lithium layer (v_n) are written as follows

$$m_1 \ddot{u}_n = K(u_{n+1}-u_n) - K(u_n-u_{n-1}) - 2xK'(v_n-u_n) - 2xK'(u_n-v_{n-1}), \tag{1a}$$

$$2xm_2 \ddot{v}_n = 2xK'(u_{n+1}-v_n) - 2xK'(v_n-u_n). \tag{1b}$$

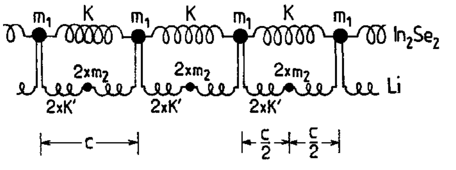

Fig. 2. Linear-chain model of lattice dynamics in the intercalated layered material $\mathrm{Li}_x\mathrm{InSe}$ ($0 \leqq x \leqq 0.5$). m_1 is the mass of each host layer and $2xm_2$ is the mass of intercalant plane. The Li planes are situated in the mid-position between two layers with a coupling force constant of $2xK'$

We look for solution to (1a) and (1b) in the form of a travelling wave of pulsation ω and wavevector $\mathbf{k}_z$. We obtain then the following equation system

$$u\{2K(\cos k_z c - 1) - 4xK' + m_1\omega^2\} + v\{2xK'[1+\exp(-ik_z c)]\} = 0, \tag{2a}$$

$$u\{2xK'[1+\exp(-ik_z c)]\} + v\{2xm_2\omega^2 - 4xK'\} = 0 \tag{2b}$$

for $x=0$, we obtain the normal relation for acoustic phonon branch in pure InSe

$$\omega_{ac}^2 = 2K(1-\cos k_z c)/m_1 \tag{3}$$

and for $x \neq 0$, the two trivial solutions are given by

$$m_1 m_2 \omega^4 - 2\omega^2\{m_1 K' + m_2[K(1-\cos k_z c) + 2xK']\} - 4xK'^2(1+\cos k_z c) + 4K'K(1-\cos k_z c) + 8xK'^2 = 0. \tag{4}$$

In the Brillouin zone centre at $\mathbf{k}=0$, (4) is reduced to

$$m_1 m_2 \omega^4 - 2K'(m_1 + 2xm_2)\omega^2 = 0$$

with solutions as

$$\omega(k=0) = 0 \tag{5a}$$

for acoustical branches, and

$$\omega_{\mathrm{int}}^2(k=0) = 2K'(m_1+2xm_2)/m_1 m_2 \tag{5b}$$

for optical branches. In the Brillouin zone boundary at $\mathbf{k}_z = \pm\pi/c$, (4) is reduced to

$$(m_1\omega^2 - 4xK' - 4K)(m_2\omega^2 - 2K') = 0 \tag{6}$$

with solutions as

$$\omega^2(k=\pi/c) = 4(K+xK')/m_1 \tag{7a}$$

for acoustical branches, and

$$\omega_{\mathrm{int}}^2(k=\pi/c) = 2K'/m_2 \tag{7b}$$

for optical branches.

We obtain one supplementary triple degenerated optical branches in comparison with the case of pure InSe. If we consider two different force constants for compression (K_c') and for shearing (K_s'), the new branch is split in one non-degenerated branch where atoms move along the z-axis and one twice degenerated where atoms move in the layer plane. These

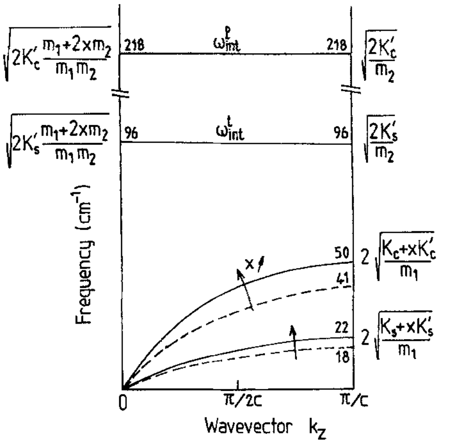

Fig. 3. Schematic phonon dispersion curves for the intercalated layered material $Li_{0.5}InSe$ (full line) and for the pristine (dashed line). The present scale corresponds to the case $K = K'$ with the masses an $m_1 = 2m_{InSe}$ and $m_2 = m_{Li}$

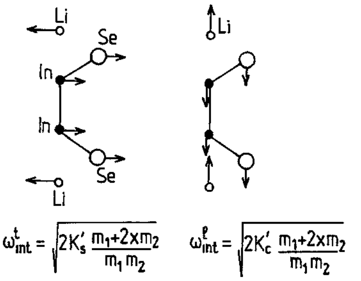

Fig. 4. Schematic representation of the atomic displacements of the new vibrational optical modes with their respective Brillouin zone centre frequency for $Li_{0.5}InSe$

branches are shown in the Fig. 3 which displays the dispersion curves of an intercalated material.

Considering the atomic motion of the new optical modes, we conclude that they are Raman and infrared active modes (Fig. 4). The extremum frequencies of this new optical phonon branch, given in (5b) and (7b) are independent of the interlayer force constant K. Of course, all the layers vibrate in phase and the layer-layer bonding is not involved. These modes are weakly dispersed along $\mathbf{k}_z$ because in our case ($m_1 = 388$ a.u. and $m_2 = 7$ a.u.) the frequency difference between the centre and the Brillouin zone boundary is less than 1%. Consequently, in the case of a possible staging effect or of a layer gliding, we cannot expect new folding modes of the optical branches.

The Brillouin zone centre frequency ω_{int} is very close to the impurity frequency mode ω_{imp} obtained when we consider the lithium as a localised impurity in the interlayer space [10]. This frequency is expressed as

$$\omega_{imp}(k=0) = [2K'/m_2]^{1/2} \tag{8}$$

Indeed, if we take into account the fact that in the present case $m_2^{(Li)} \ll m_1^{(In_2Se_2)}$, then (5b) becomes approximately as follows

$$\omega_{int}(k=0) \approx [2K'/m_2]^{1/2} \tag{9}$$

In the ELCM, the $\omega_{int}(k=0)$ modes are not sensitive to the inserted atom concentration. This result is due to the fact that these vibrations are only characterized by the lithium layer bonding. On other hand, the Brillouin zone boundary frequencies of the acoustic branches are dependent of the inserted atom concentration as shown by (7a). Indeed, these modes correspond to the motion of each adjacent host layers in opposite phase and the layer-layer bonding is strongly involved. With lithium concentration increase, we can expect an increase of the layer-layer bonding, and consequently an increase of the Brillouin zone boundary acoustic frequencies.

To calculate approximately the frequencies of the intercalant modes, we can assume that lithium-layer and layer-layer force constants have the same value ($K = K'$). In this assumption, the frequency of the Brillouin zone boundary acoustic mode of the pure γ-InSe is sufficient to determine from (3) these force constants. In the ε-InSe polytype these acoustic branches are folded, but only the TA folded mode or the rigid layer mode has been observed experimentally in Raman scattering at 18 cm^{-1} [10]. But, if we consider the (3) for the two different force constants K_s and K_c, we show the validity of the following relation

$$K_s^{1/2}\,\omega_{ac}^{LA}(k_z=\pi/c) = K_c^{1/2}\,\omega_{ac}^{TA}(k_z=\pi/c)$$

and using the force constant ratio $K_c/K_s = 5.15$ determined by Alivea et al. [9], we deduce an approximative value for $\omega_{LA}(k_z=\pi/c)$ of 41 cm^{-1}. Then considering (3) and (5b) we can write the intercalation mode frequency as a function of the acoustical mode frequency as

$$w_{int} = \omega_{ac}[(m_1 + 2xm_2)/2m_2]^{1/2}$$

and therefore, calculate the frequencies of the new optical phonons in Brillouin zone centre; for $x = 0.5$ we obtain $\omega_{int} = 5.33\,\omega_{ac}$. Finally the new optical phonon are determined at 96 and 218 cm^{-1} for the inner layer and the z-axis motion modes respectively. These values are weakly dependent with the intercalant concentration and are comparable with those obtained by Kunc et al. [5–7] in DTE at 97 cm^{-1} for the inner layer mode. The z-axis modes at 230 and

430 cm^{-1} have been calculated for an intercalant in OS and TS respectively.

In the same approximation ($K = K'$) the Brillouin zone boundary mode frequencies are multiplied by a factor $(1+x)^{1/2}$ which can vary between 1 and 1.22 in the limit of our model for the concentration range $0<x<0.5$. In the case of the possible zone folding, we can expect new Raman peaks between 18 and 50 cm^{-1} as shown in Fig. 3 where the dispersion curves are calculated for $\mathrm{Li}_x\mathrm{InSe}$ in the ELCM approximation for $K = K'$.

3. Experimental evidence of intercalation modes

Using Raman scattering experiments, the presence of intercalation modes in the phononic spectrum has been evidenced. Lithium intercalated InSe samples have been prepared by spontaneous reaction for 200 h in *n*-butyl-lithium dissolved in hexane forming a 1.6 *M* solution. The average lithium concentration into the single crystal is estimated at $x = 0.5$.

Figure 5 shows the Raman spectra of pure (curve a) and $\mathrm{Li}_{0.5}\mathrm{InSe}$ (curve b) at 5 *K*. These spectra are obtained in the quasi-backscattering configuration on the basal plane, using an argon ion laser line of 5 mW power at 514.5 nm. All other experimental details have been described elsewhere [2]. For a relatively low lithium concentration ($x<1$), the Raman spectrum of Fig. 5b can be regarded as the result of three features: the unchanged phonon spectrum of InSe with its normal modes at 117.5, 181.5 and 232 cm^{-1}, the coupling phonon-plasmon spectrum which displays two broad bands at 90 ± 2 and 204 ± 5 cm^{-1} [3], and the new peaks measured at 21 ± 0.5, 62 ± 2, 102 ± 3 and 388 ± 3 cm^{-1}.

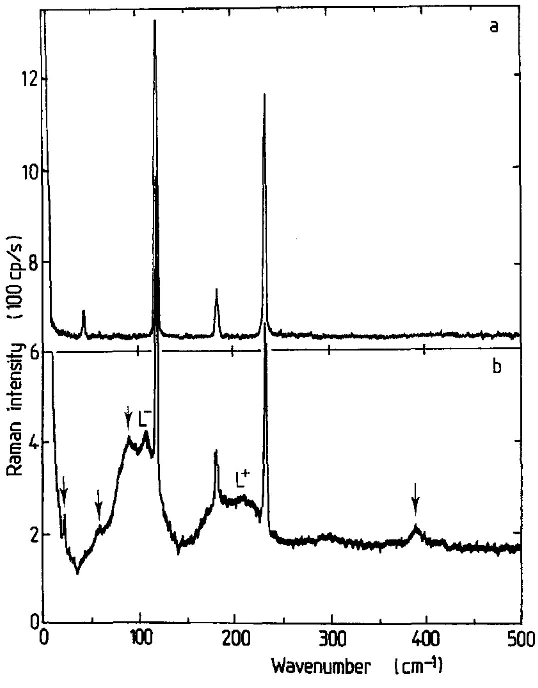

Fig. 5a and b. Raman scattering spectra at 5 K of (**a**) pure InSe, and (**b**) $\mathrm{Li}_{0.5}\mathrm{InSe}$ intercalated by the *n*-butyl-method. A laser excitation line of 5 mW at 514.5 nm, and an average of 23 scans was used in this experiment

By comparison of the experimental results with the calculated mode frequencies given by the ELCM and those obtained by the DTE, reasonable attributions of the modes are as follows. The peaks at 21 and 62 cm^{-1} are probably due to the folded transverse and longitudinal acoustic branches. The origin of this folding is unknown, but a simple gliding of the layers upon lithium insertion may be sufficient to induce a superlattice structure along the *z*-axis. We assign the peak at 100 cm^{-1} as the transverse optical intercalation mode $\omega^{t}_{\mathrm{int}}(\mathrm{TO})$ which has been estimated at 96 cm^{-1} with the ELCM calculation, and at 97 cm^{-1} for a tetrahedral or octahedral site occupancy using the DTE calculation. The observed band at 388 cm^{-1} can be attributed to the longitudinal optical intercalation mode $\omega^{l}_{\mathrm{int}}(\mathrm{LO})$ for which a transverse optical component has been calculated at 218 cm^{-1} in the ELCM. The second type of calculation gives this latter at 230 cm^{-1} for an octahedral site, and at 430 cm^{-1} for a tetrahedral site.

In the case of the optical mode at low frequency which describes an oscillating movement of the intercalant along the layer plane, the disagreement is probably due to an under-estimation of the Li-layer shearing force constant. The ELCM has shown that the effect induced by the site position of the intercalant is negligible for the determination of this mode frequency. In opposite, in the case of the high frequency mode which describes an oscillation of the intercalant perpendiculary to the layer plane, the site position influences strongly the mode frequency as shown in the calculation of Kunc et al. [6]. The calculated frequency at 430 cm^{-1}, in the case of a tetrahedral site is the nearest value of the experimental data. This result indicates probably that the most favourable insertion sites of lithium are the tetrahedral positions.

4. Conclusion

We have studied lattice dynamics in intercalated InSe by a simple one-dimensional linear-chain model. This model give us a basic framework and fundamental concept for the attribution of new peaks appearing in Raman scattering spectroscopy.

We are grateful to Drs. R. Sekine and K. Kunc for fruitful discussions. We thank also Dr. A. Chevy who kindly provides InSe single crystals.

References

1. See for example: Legrand, A.P., Flandrois, S (eds.) Chemical physics of intercalation. NATO-ASI Series B **172**. New-York: Plenum 1987
2. Julien, C., Jouanne, M., Burret, P.A., Balkanski, M.: Solid State Ionics, **28–30**, 1167 (1988)
3. Julien, C., Jouanne, M., Burret, P.A., Balkanski, M.: Mat. Sci. Eng. B **3** 33 (1989)
4. Burret, P.A., Julien, C., Jouanne, M., Balkanski, M.: Mat. Res. Soc. Proc., Vol. **135** p. 473 Nazri, G., Huggins, R.A., Schriver, R., Wu, P. (eds.) (1989)
5. Kunc, K., Zeyher, R.: Europhys. Lett, **7** 611 (1988)
6. Kunc, K., Zeyher, R., Molinari, E.: Proceedings of Varsaw Semiconductor Conference 1988 (in press)
7. Kunc, K.: Private communication, 1988
8. Wieting, T.J., Verble, J.L.: In Physics and chemistry of materials with layered structure. Wieting, T.J., Schlüter, M. (eds.), Vol. 3, p. 321. Dordrecht: D. Reidel 1979
9. Sekine, T., Balkanski, M.: Mat. Sci. Eng. B **1**, 155 (1988)
10. Alivea, L.N., Belen'kii, G.L., Reshina, I.I., Salaev, Y., Shteinshraiser, V.Y.: Sov. Phys. Solid State, **21** (1979) 90

P.A. Burret, M. Jouanne, C. Julien
Laboratoire de Physique des Solides
Université Pierre et Marie Curie
associé au CNRS
4, Place Jussieu
F-75252 Paris Cedex 05
France