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## Theoretical and experimental study of Raman scattering in mixed $(\text{MoS}_2)_x(\text{MoSe}_2)_{1-x}$ layered crystals

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**Abstract.** Raman scattering in mixed  $\text{MoS}_2/\text{MoSe}_2$  layer type crystals was investigated in this work. The change of intensities and positions of bands for in-plane  $E_{2g}^1$  and out-of-plane  $A_{1g}$  vibrations as functions of the “concentration” inherent to corresponding type layers has been studied. Estimation of interlayer interaction was obtained from comparison of experiment and theory, and effect of this interaction on the frequency of intralayer phonon was studied.

**Keywords:** Raman scattering, interlayer interaction, phonon, vibration, layered crystals.

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### 1. Introduction

Spectroscopic studying the layer type crystals was performed for a long time. It began in the early 70-th of the last century. Investigations were related with both the electron and vibration properties of these crystals. Study of phonons was very intensively made for different types of layered crystals, GaSe [1], GaS [2],  $\text{MoS}_2$  [3-5],  $\text{As}_2\text{S}_3$  [6],  $\text{MoSe}_2$ ,  $\text{MoW}_2$  [7], *etc.* and some models explaining the observed features, in particular Davydov’s splitting effect, were proposed.

The new period of activity in studying these crystals arose when technological possibility appeared, using the method by Novoselov *et al.* for graphene, which enabled to prepare a very thin crystal structure having 1 to 10 atomic layers [8]. Especially perspective in this plan are layered crystals  $\text{MoS}_2$  and  $\text{MoSe}_2$  showing new spectroscopic features, if the crystal structure consists of only several  $n = 1 \dots 6$  atomic layers [7, 9] (see also numerous references cited there).

The electron band structure of these crystals differs from the bulk one, and they demonstrate very intensive luminescence. The number of works in which electron

and phonon properties of such type crystal structures are studied using the spectroscopic methods, grows significantly for the last years.

Recently, detailed study of vibration spectra of  $\text{MoS}_2$  layer crystals consisting of several layers,  $n = 1 \dots 6$  and analysis of its results were made in [9]. The authors observed strong signals of the in-plane ( $E_{2g}^1$ ) and out-of-plane ( $A_{1g}$ ) Raman modes of all 6 layers. These modes exhibited a well-defined thickness dependence, with the two modes shifting away from each other in frequency with increasing the thickness. The behavior of frequency shifts with changing the layer thickness, as it was emphasized by the authors [9], cannot be explained solely in terms of weak van der Waals (vdW) interlayer interaction.

The spectrum as a function of the film thickness has several features. It is noted that most strikingly that more low frequency  $E_{2g}^1$  vibration softens (red shifts), while the high frequency  $A_{1g}$  vibration stiffens (blue shifts) with increasing the sample thickness. For the films consisting of four or more layers, the frequencies of both modes converge to the bulk values. Also, the rate

of frequency change is twice as large for the  $A_{1g}$  as for  $E_{2g}^1$  mode. The similar features were recently observed, too. The vibrations of bulk materials built up from vdW-bonded layers are often analyzed in terms of the work [10].

The vibrations of bulk materials built up from vdW-bonded layers are often analyzed in terms of the two-dimensional layers from which they are formed [1, 3, 5]. Within a classical (traditional) model for coupled harmonic oscillators [11],  $E_{2g}^1$ , and  $A_{1g}$  modes are expected to stiffen as additional layers are added to form the bulk material from individual layers, because the interlayer vdW interactions increase the effective restoring forces acting on the atoms. While the shift of  $A_{1g}$  mode was observed in experiments of the work [9] with increasing the layer number agrees with prediction, behavior of the  $E_{2g}^1$  mode does not. The failure of the model could indicate that the implicit assumption that stacking does not affect intra-layer bonding is incorrect.

But in reality, even weak interlayer interaction in crystals can affect intra-layer bonding and lattice dynamics. It can be explained at least particularly on the base of results obtained in works [12-14] where Fermi-Davydov (FD) resonance in molecular type crystals was considered. Positions of bands and their intensities depend on the weak vdW intermolecular interaction and intramolecular frequencies are renormalized. Indeed, as a result of intramolecular interaction between fundamental vibrations and overtones (combination tones) of molecule, two strong bands (Fermi resonance doublet) arise with frequencies  $\omega_f$ , and  $\omega_g$ . In crystal, due to weak intermolecular interaction and exchange by excitations, even with one molecule per crystal unit cell two type of Davydov terms appear: diagonal,  $D^{ff}$ ,  $M^{ff}$ ,  $D^{gg}$ ,  $M^{gg}$  and non-diagonal  $D^{gf}$ ,  $M^{gf}$ . The diagonal terms result in shift like to all spectral bands, but the non-diagonal ones give rise to repulsion of new crystal states. Therefore, the shift of high- and low-frequency Fermi-doublet components should be in different sides. Similar facts were observed in experiments [9, 10]. A more complicated case in particular with taking into account of Fermi-Davydov resonance and strong interaction of H-bond vibrations with lattice phonons was later theoretically considered in [15].

In recent experiments, when studying mixed layer type crystals  $\text{MoS}_2/\text{MoSe}_2$  new features related with complex variation of spectrum were observed in [10]. The problem related with influence of intra-interlayer interactions looks in this case especially complex for both the position of bands and their intensities, and it includes as a particular case the aspects noted in [9]. Therefore, we consider first a more general task for mixed crystals, and then the features related with thin layer type crystals will be discussed.

## 2. Intensity of Raman scattering

RS intensity can be expressed by imaginary part of Fourier component Green function in the tensor of the crystal susceptibility  $\chi_{\alpha,\beta}$  [16, 17], where Hamiltonian describing the interaction of electromagnetic (EM) field with crystal looks as follows

$$H_{\text{int}} = -\frac{1}{V} \sum_{k,\lambda,k',\lambda',\alpha,\beta} \bar{e}_\alpha(k,\lambda) \bar{e}_\beta^*(k',\lambda') P_{-k,\lambda} P_{-k',\lambda'}^+ \chi_{\alpha,\beta}(k'-k) = -\frac{1}{V} \sum_{k,\lambda,k',\lambda'} P_{-k,\lambda} P_{-k',\lambda'}^+ \chi_{k,\lambda,k',\lambda'}, \quad (1)$$

$$\chi_{k,\lambda,k',\lambda'} = \sum_{\alpha,\beta} \bar{e}_\alpha(k,\lambda) \bar{e}_\beta^*(k',\lambda') \chi_{\alpha,\beta}(k'-k);$$

$$\chi_{-k,\lambda,-k',\lambda'} = \chi_{k,\lambda,k',\lambda'}^* = \chi_{k',\lambda',k,\lambda}, \quad (2)$$

$$\chi_{\alpha,\beta}(\vec{Q} = \vec{k}' - \vec{k}) = \chi_{\alpha,\beta}^*(-Q) = \sum_n \chi_{\alpha,\beta}(\vec{n}) \exp(-i\vec{Q}\vec{n}), \quad (3)$$

$$P_{k,\lambda} = \frac{1}{\sqrt{2}} (a_{k,\lambda}^+ - a_{-k,\lambda}), \quad A_{k,\lambda} = \frac{1}{\sqrt{2}} (a_{k\lambda} + a_{-k,\lambda}^+).$$

Here,  $\omega_{k,\lambda}$ ,  $\bar{e}_\alpha(k,\lambda)$  are the photon frequency and  $\alpha$ -component of the electric field unit vector;  $a_{k,\lambda}^+$ ,  $a_{k,\lambda}$  – Bose operators of creation and annihilation of electric field, respectively;  $P_{k,\lambda}$  and  $A_{k,\lambda}$  – operators of momentum and potential of EM field, correspondingly, satisfying the commutation relations  $[A_{k,\lambda}; P_{k',\lambda'}] = \delta_{k,k'} \delta_{\lambda,\lambda'}$ .

In the layer type crystal where different layers can have various properties, two indexes ( $l$ ,  $n$ ) should be used to numerate unit cells of the crystal: the first index ( $l$ ) points out the number of layer and the other one ( $n$ ) – the number of the unit cell in layer. For convenience, the wave vector is also presented by two components oriented in layer,  $\vec{Q}_n$ , and normal to layer,  $\vec{Q}_l$ , correspondingly, so that  $\vec{Q} = \vec{Q}_l + \vec{Q}_n$ . Then,

$$\chi_{\alpha,\beta}(\vec{Q} = \vec{k}' - \vec{k}) = \sum_{n,l} \chi_{\alpha,\beta}(\vec{n} + \vec{l}) \times \exp[-i(\vec{Q}_l + \vec{Q}_n)(\vec{n} + \vec{l})] = \sum_{n,l} \chi_{\alpha,\beta}(\vec{n} + \vec{l}) \exp[-i(\vec{n}\vec{Q}_n + \vec{l}\vec{Q}_l)]. \quad (5)$$

The value  $\chi_{\alpha,\beta}(\vec{n} + \vec{l})$  can be presented as expansion in series on deviation of atoms in  $l$  layer,  $u_{n,k,\alpha}^l$ , from equilibrium position, which are then expressed by normal coordinates of phonon operators,  $\phi_{Q_n,s_l}^l$ . Here,  $s_l$  are phonon quantum states of layer  $l$ . Using Eqs. (5) and (2), the following expression for susceptibility of crystal can be obtained:

$$\chi_{k,\lambda,k',\lambda'} = \sqrt{N_0} \sum_{l,s_l} \chi_{k\lambda,k'\lambda'}^l(Q_n, s_l) \exp(-ilQ_l) \phi_{Q_n, s_l}^l, \quad (6)$$

$N_0$  is the number of unit cell in layer.

Because the  $N_{s_l}$  layers with quantum states  $s_l$  are arbitrary distributed between full numbers of crystal layers, the  $N_l$  response of crystal on incident light will be averaged. Therefore, the expression (6) describing susceptibility should be averaged on their distribution. The probability that each layer at the same time will occupy each "layer cell" in crystal is equal,  $c_{s_l} = N_{s_l} / N_l$ . So, we obtain situation that the same response on the incident light is carried out by  $N_l$  crystal layers but with the probability  $c_{s_l}$ . Because all layers are now identical, the susceptibility is independent on  $l$ , i.e.,  $\chi_{k,\lambda,k',\lambda'}^l(Q_n, s_l) = \chi_{k,\lambda,k',\lambda'}(Q_n, s_l)$ . This allows making simplification of Eq. (6) as follows

$$\begin{aligned} \chi_{k,\lambda,k',\lambda'} &= \sqrt{N_0} \sum_{l,s_l} c_{s_l} \chi_{k,\lambda,k',\lambda'}(Q_n, s_l) \exp(-ilQ_l) \times \\ &\times \frac{1}{\sqrt{N_l}} \sum_p \exp(ipl) \phi_{p,Q_n, s_l} = \\ &= \sqrt{N_0 N_l} \sum_{s_l} c_{s_l} \chi_{k,\lambda,k',\lambda'}(Q_n, s_l) \phi_{Q_l, Q_n, s_l}, \quad (7) \end{aligned}$$

For conveniency, we introduce  $c_{s_l} \chi_{k,\lambda,k',\lambda'}(Q_n, s_l) = \tilde{\chi}_{s_l}$ , where the index  $s_l$  has a double meaning:  $l$  points out on the type of layers forming the crystal and  $s_l = \{s_l^1, s_l^2, \dots\}$  characterize the different vibration states in this layer.

As it was noted above, the intensity of RS can be expressed by Fourier component Green function from the tensor of susceptibility of crystal, and in our case the intensity of light scattering by one unit cell is described by the following expression

$$\begin{aligned} I_{p',\lambda',p,\lambda} &\sim -\frac{1}{\pi} [1+n(\omega)] \times \\ &\times \text{Im} \left\{ \left\langle \left\langle \chi_{p',\lambda',p,\lambda}(t); \chi_{p',\lambda',p,\lambda}^+(0) \right\rangle \right\rangle_{\omega} \right\} = \\ &= -\frac{1}{\pi} [1+n(\omega)] \text{Im} \left\{ \sum_{s_l, s_{l'}} \tilde{\chi}_{s_l} \tilde{\chi}_{s_{l'}}^* \left\langle \left\langle \phi_{Q, s_l}(t); \phi_{Q, s_{l'}}^+(0) \right\rangle \right\rangle_{\omega} \right\}, \quad (8) \end{aligned}$$

where values in brackets are Fourier components of retarded Green functions

$$G_{s_l, s_{l'}}(Q, \omega) = \left\langle \left\langle \phi_{Q, s_l}(t); \phi_{Q, s_{l'}}^+(0) \right\rangle \right\rangle_{\omega}. \quad (9)$$

It is known from the group theory that intermixing by anharmonicity of states in particular intralayer states

are possible, if they have the same symmetry. Experiments show that, for MoS<sub>2</sub> and MoSe<sub>2</sub> layer crystals having  $D_{6h}$  space group, the most strong bands observed in RS spectra correspond to  $A_{1g}$  and  $E_{2g}$  symmetries. In this paper, we consider the case of mixing the states in mixed crystals with the noted symmetries. In other words, only two types of layers  $l=0$  and  $l=1$  corresponding to MoS<sub>2</sub> and MoSe<sub>2</sub>, respectively, are taken into consideration, and their vibrations should have an identical symmetry,  $A_{1g}$  (or  $E_{2g}$ ). Then, for the given case, the intensity of RS is described by Eq. (8), which looks as follows

$$\begin{aligned} I_{p',\lambda',p,\lambda} &\sim -\frac{1}{\pi} [1+n(\omega)] \times \\ &\times \text{Im} \left\{ \tilde{\chi}_{s_0} \tilde{\chi}_{s_0}^* G_{s_0 s_0}(\omega) + \tilde{\chi}_{s_0} \tilde{\chi}_{s_1}^* G_{s_0 s_1}(\omega) + \tilde{\chi}_{s_1} \tilde{\chi}_{s_0}^* G_{s_1 s_0}(\omega) + \tilde{\chi}_{s_1} \tilde{\chi}_{s_1}^* G_{s_1 s_1}(\omega) \right\}, \quad (10) \end{aligned}$$

In Eq. (10), we took into account that ( $Q \rightarrow 0$ ) and used designation  $G_{s_l s_{l'}}(Q \rightarrow 0, \omega) = G_{s_l s_{l'}}(\omega)$ .

### 3. Hamiltonian and equations for Green functions of layer crystal vibrations

Hamiltonian of layer crystal in the secondary quantum representation (SQR) is written as follows

$$\begin{aligned} H &= H_0 + H_{\text{int}} = \sum_{l, q, s_l} \omega_{q, s_l}^l b_{q, s_l}^+ b_{q, s_l}^l + \\ &+ \frac{1}{2} \sum_{q, s_l, s_{l'}, l \neq l'} \tilde{V}^n \left( \begin{matrix} l, l' \\ q, s_l, s_{l'} \end{matrix} \right) \phi_{q, s_l}^l \phi_{q, s_{l'}}^{l'}, \quad (11) \end{aligned}$$

where  $\omega_{q, s_l}^l$ ,  $b_{q, s_l}^+$ ,  $b_{q, s_l}^l$  are phonon frequency and creation-annihilation operators of  $l$  layer phonons. The normal coordinate  $\phi_{q, s_l}^l$  and momentum  $\pi_{q, s_l}^l$  look as follows

$$\phi_{q, s_l}^l = \frac{1}{\sqrt{2}} (b_{q, s_l}^l + b_{-q, s_l}^{+l}), \quad \pi_{q, s_l}^l = \frac{1}{\sqrt{2}} (b_{q, s_l}^{+l} - b_{-q, s_l}^l). \quad (12)$$

The first sum in Eq. (11),  $H_0$ , describes the system of non-interacting layer's oscillators but the second term is responsible for interlayer interaction of phonons.

Fourier components of Green functions (GF) describing the RS by averaged layer crystal are given in Eq. (15), but now we will study the GF of a more general form

$$G_{k, s_l, k', s_{l'}}(t) = \left\langle \left\langle \phi_{k, s_l}^l(t); \phi_{k', s_{l'}}^{l'}(0) \right\rangle \right\rangle. \quad (13)$$

The equation for such GF looks as follows

$$i \frac{\partial}{\partial t} G_{k,s_l,k',s_{l'}}(t) = \delta(t) \left\langle \left[ \phi_{k,s_l}^l(0); \phi_{k',s_{l'}}^{+l'}(0) \right] \right\rangle + \left\langle \left\langle i \frac{\partial}{\partial t} \phi_{k,s_l}^l(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle. \quad (14)$$

The equation relating Fourier components of similar type GF,  $\left\langle \left\langle \phi_{k,s_l}^l(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle_{\omega}$ , can be written as follows

$$\left[ \omega^2 - \left( \omega_{k,s_l}^l \right)^2 \right] \left\langle \left\langle \phi_{k,s_l}^l(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle_{\omega} = -\omega_{k,s_l}^l \left\{ -\delta_{k,k'} \delta_{l,l'} \delta_{s_l,s_{l'}} - \sum_{s_r, l'' (\neq l)} \tilde{V}_{(s_l, s_r, k)}^{(l, l'')} \left\langle \left\langle \phi_{k,s_r}^{l''}(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle_{\omega} \right\}. \quad (15)$$

It is seen that nonzero solution can be obtained, if *intra-layer* wave vectors are equal,  $k = k'$ , but concerning interlayer interaction the situation is more complicate because layers in crystal are arbitrary distributed. Therefore, the response of crystal on the incident radiation will be averaged on all possible distributions of layers interacting with one another. Averaging Eq.(15) on all  $l''$  and  $l$  layers, phonons of which characterizes  $s_l, s_{l''}$  quantum states, gives rise to appearance of probabilities  $c_{s_l} = N_{s_l} / N_l$  and  $c_{s_{l''}} = N_{s_{l''}} / N_l$ . Therefore, Eq. (15) is transformed into the following one

$$\left[ \omega^2 - \left( \omega_{k,s_l}^l \right)^2 \right] \left\langle \left\langle \phi_{k,s_l}^l(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle_{\omega} = -\omega_{k,s_l}^l \left\{ -\delta_{k,k'} \delta_{l,l'} \delta_{s_l,s_{l'}} - \sum_{s_r, l'' (\neq l)} c_{s_l} c_{s_r} \tilde{V}_{(s_l, s_r, k)}^{(l, l'')} \left\langle \left\langle \phi_{k,s_r}^{l''}(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle_{\omega} \right\}. \quad (16)$$

In this approximation, we have the homogeneous crystal structure fully filled with identical layers of  $(l, s_l)$  or  $(l'', s_{l''})$  types, but interlayer interaction become smaller and depend on the coefficients  $c_{s_l} c_{s_{l''}}$ . This situation is very similar to that studied in molecular crystal having several molecules in the unit cell and quasi-degenerated levels in molecules [12-15], because after averaging we obtain a new layer crystal, in which different type layers  $(l, s_l)$  and  $(l'', s_{l''})$  can be considered as forming complex double layer “elementary cell”, but with more weak interlayer interaction. For a homogenous crystal structure, one can write,  $\tilde{V}_{(s_l, s_r, k)}^{(l, l'')} = \tilde{V}_{(s_l, s_r, k)}^{(l-l'')}$ . Besides, in this approximation in Eq. (16) all functions depend only on the difference

between layers  $l-l''$ , therefore the following Fourier transformation can be made.

$$\left\langle \left\langle \phi_{k,s_l}^l(t); \phi_{k',s_{l'}}^{+l'}(0) \right\rangle \right\rangle_{\omega} = \frac{1}{N} \sum_p G_{s_l, k, s_{l'}, k'}(p, \omega) \exp[ip(l-l')], \quad (17a)$$

$$\tilde{V}_{(s_l, s_{l'}, k)}^{(l-l'')} = \frac{1}{N_l} \sum_p V_{s_l, s_{l'}}(p, k, \omega) \exp[ip(l-l'')], \quad (17b)$$

$$\delta_{l,l'} = \frac{1}{N} \sum_p \exp[ip(l-l')]. \quad (18)$$

Then, Eq. (16) can be written in a more simple form (the conservation law for layer wave vectors,  $k = k'$ , is taken into account)

$$\sum_{s_r} \left\{ \left( \omega^2 - \omega_{k,s_r}^2 \right) \delta_{s_l, s_r} + \omega_{k,s_l} c_{s_l} c_{s_r} \tilde{V}_{(s_l, s_r)}^{(k,p)} \right\} \times \times G_{s_r, s_{l'}}(p, k, \omega) = \omega_{k,s_l} \delta_{s_l, s_{l'}}. \quad (19)$$

In Eq. (19), the index  $s_l$  similar to Eqs. (7)-(13) has the double meaning: i)  $l$  points out the character of layer, ii)  $s = \{s_l^1, s_l^2, \dots\}$  marks the type of vibrations in this layer, if several vibrations in the given layer are considered. We have noted in Section 2 that only two types of layers  $l=0$  and  $l=1$  corresponding to MoS<sub>2</sub> and MoSe<sub>2</sub>, respectively, are taken into consideration and only one of layer vibrations that have an identical symmetry,  $A_{1g}$  (or  $E_{2g}$ ) are studied. The fundamental vibrations can be mixed by fourth order anharmonicity of layer but this value is very low and in current investigation is omitted.

Taking into account that designations  $s_l = s_0, s_1$  are, respectively, related with MoS<sub>2</sub> and MoSe<sub>2</sub> layer types, two pairs of equations are obtained.

a)  $s_l = s_0$ , the first system of equations looks as follows:

$$\Delta_{s_0 s_0} G_{s_0 s_0} + D_{s_0 s_1} G_{s_1 s_0} = \omega_{k, s_0}, \quad (s_l = s_0), \quad (20a)$$

$$D_{s_1 s_0} G_{s_0 s_0} + \Delta_{s_1 s_1} G_{s_1 s_0} = 0, \quad (s_l = s_1), \quad (20b)$$

b)  $s_l = s_1$ , the second system of equations looks as follows:

$$\Delta_{s_0 s_0} G_{s_0 s_1} + D_{s_0 s_1} G_{s_1 s_1} = 0, \quad (s_l = s_0) \quad (21a)$$

$$D_{s_1 s_0} G_{s_0 s_1} + \Delta_{s_1 s_1} G_{s_1 s_1} = \omega_{k, s_1}, \quad (s_l = s_1) \quad (21b)$$

where designations in Eqs. (20a, b) and Eqs. (21a, b) have the following look:

$$\Delta_{s_l s_l'} = (\omega^2 - \omega_{k, s_l'}^2) \delta_{s_l s_l'} + \omega_{k, s_l} c_{s_l} c_{s_l'} \tilde{V}_{(s_l, s_l')}^{(k, p)}, \quad (22a)$$

$$D_{s_l s_l'} = \omega_{k, s_l} c_{s_l} c_{s_l'} \tilde{V}_{(s_l, s_l')}^{(k, p)}. \quad (22b)$$

In the following consideration, we will omit for convenience the indexes  $k, p$  describing the components of the wave vector for crystal excitations. As it is seen from Eqs. (7), both wave vectors are related with components of exciting radiation  $\vec{Q} = \vec{Q}_l + \vec{Q}_n \rightarrow 0$  where interlayer,  $k = \vec{Q}_n$ , and normal to layer,  $p = \vec{Q}_l$ , components respectively. Solutions of Eqs. (20a, b)-(21a, b) are as follows

$$G_{s_0 s_0} = \frac{\omega_{s_0} \Delta_{s_1 s_1}}{\Delta}, \quad G_{s_1 s_0} = \frac{-\omega_{s_0} D_{s_1 s_0}}{\Delta}; \quad (23a)$$

$$G_{s_1 s_1} = \frac{\omega_{s_1} \Delta_{s_0 s_0}}{\Delta}, \quad G_{s_0 s_1} = \frac{-\omega_{s_1} D_{s_0 s_1}}{\Delta}; \quad (23b)$$

where written below designation was used

$$\Delta = \Delta_{s_0 s_0} \Delta_{s_1 s_1} - D_{s_1 s_0} D_{s_0 s_1}. \quad (24)$$

Insertion of Eqs. (23a, b) and (24) into Eq. (10) gives rise to the following expression for the spectral dependence of RS intensity

$$I_{p', \lambda', p, \lambda} \sim -\frac{1}{\pi} [1 + n(\omega)] \times \times \text{Im} \left\{ \frac{1}{\Delta} \left[ \tilde{\chi}_{s_0} \tilde{\chi}_{s_0}^* (\omega_{s_0} \Delta_{s_1 s_1}) + \tilde{\chi}_{s_0} \tilde{\chi}_{s_1}^* (-\omega_{s_1} D_{s_0 s_1}) + \tilde{\chi}_{s_1} \tilde{\chi}_{s_0}^* (-\omega_{s_0} D_{s_1 s_0}) + \tilde{\chi}_{s_1} \tilde{\chi}_{s_1}^* (\omega_{s_1} \Delta_{s_0 s_0}) \right] \right\}. \quad (25)$$

For simplicity, we will suppose that the RS tensor components are real,  $\tilde{\chi}_{s_l} = \tilde{\chi}_{s_l}^*$ . Now, to take into account the damping of phonon excitations, we will suppose the frequency to be a complex value,  $\omega \rightarrow \omega + i\gamma$ , therefore, all the values depending on frequency in numerator and denominator become the complex ones, in particular

$$\Delta_{s_0 s_0} = (\omega^2 - \gamma^2 - \omega_{s_0}^2 + D_{s_0 s_0}) + i2\omega\gamma = \tilde{\Delta}_{s_0 s_0} + i2\omega\gamma, \quad (26a)$$

$$\Delta_{s_1 s_1} = (\omega^2 - \gamma^2 - \omega_{s_1}^2 + D_{s_1 s_1}) + i2\omega\gamma = \tilde{\Delta}_{s_1 s_1} + i2\omega\gamma. \quad (26b)$$

Therefore, the final expression for intensity of RS can be written as follows

$$I_{p', \lambda', p, \lambda} \sim \frac{1}{\pi} [1 + n(\omega)] \times \frac{2\omega\gamma \left\{ \omega_{s_0} \left[ (\tilde{\chi}_{s_0} \tilde{\Delta}_{s_1 s_1} - \tilde{\chi}_{s_1} D_{s_0 s_1})^2 + 4\tilde{\chi}_{s_0}^2 \omega^2 \gamma^2 \right] + \omega_{s_1} \left[ (\tilde{\chi}_{s_1} \tilde{\Delta}_{s_0 s_0} - \tilde{\chi}_{s_0} D_{s_0 s_1})^2 + 4\tilde{\chi}_{s_1}^2 \omega^2 \gamma^2 \right] \right\}}{\left[ \tilde{\Delta}_{s_0 s_0} \tilde{\Delta}_{s_1 s_1} - 4\omega^2 \gamma^2 - D_{s_1 s_0} D_{s_0 s_1} \right]^2 + \left[ 2\omega\gamma (\tilde{\Delta}_{s_0 s_0} + \tilde{\Delta}_{s_1 s_1}) \right]^2} \quad (27)$$

It should be taken into consideration that in Eq. (27),  $\tilde{\chi}_{s_l} = c_{s_l} \chi_{k, \lambda, k', \lambda'} (Q_n \rightarrow 0, s_l) = c_{s_l} \chi_{s_l}$ , according to Eq. (7), therefore, the effective tensor of scattering  $\tilde{\chi}_{s_l}$  is changed with the ‘‘concentration’’ of the given sort of layers and real parameter is  $\chi_{s_l}$ . Eq. (27) shows that RS intensity has an enough complicated dependence on the frequency  $\omega$ , relation between concentrations of different type layers  $c_{s_l}$  and interaction between layers  $\tilde{V}_{s_l, s_l'}$ . The resonance frequencies are obtained from the first term in the denominator of Eq. (27) (if  $\gamma \rightarrow 0$ ) and according to Eqs. (26a, b) are equal

$$\omega^2 - \gamma^2 = \frac{1}{2} \left\{ \left[ (\omega_{s_0}^2 - D_{s_0 s_0}) + (\omega_{s_1}^2 - D_{s_1 s_1}) \right] \pm \sqrt{\left[ (\omega_{s_0}^2 - D_{s_0 s_0}) - (\omega_{s_1}^2 - D_{s_1 s_1}) \right]^2 + 16\omega^2 \gamma^2 + 4D_{s_0 s_1} D_{s_1 s_0}} \right\}. \quad (28)$$

In the case when crystals MoS<sub>2</sub> or MoSe<sub>2</sub> consist of only identical layers, some correction to resulting Eq. (28) should be made, because mixing the states by anharmonicity at corresponding their symmetries are possible.

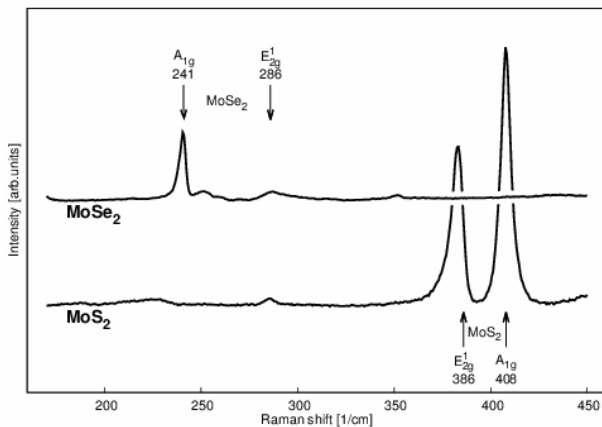
#### 4. Mixing of crystal states with identical layers and discussion of experiments

The estimation of interlayer interaction parameters can be made on the base of results of theoretical calculations for phonons in one-layer and bulk MoS<sub>2</sub> crystal obtained in work [20]. The actual phonon frequencies for one-layer MoS<sub>2</sub>,  $D_{3h}$  point group symmetry, are as follows  $\omega_{A_1'} \approx 410.3 \text{ cm}^{-1}$  and  $\omega_{E_1'} = 391.7 \text{ cm}^{-1}$ , but the corresponding ones for bulk MoS<sub>2</sub> with  $D_{6h}$  point group have very close values  $\omega_{A_{1g}} = 412 \text{ cm}^{-1}$  and  $\omega_{E_{2g}} = 387.8 \text{ cm}^{-1}$  to the former phonon pair. It means that change of frequencies due to interlayer interaction is close to 3-5  $\text{cm}^{-1}$ , if one takes into consideration some mistakes in numerical calculations. But experiments show that observed for *one-layer* frequencies are  $\omega_{A_1'} \approx 404 \text{ cm}^{-1}$  and  $\omega_{E_1'} \approx 383 \text{ cm}^{-1}$ , which are obviously lower than those predicted theoretically. One of the reasons can be anharmonic interaction that is are

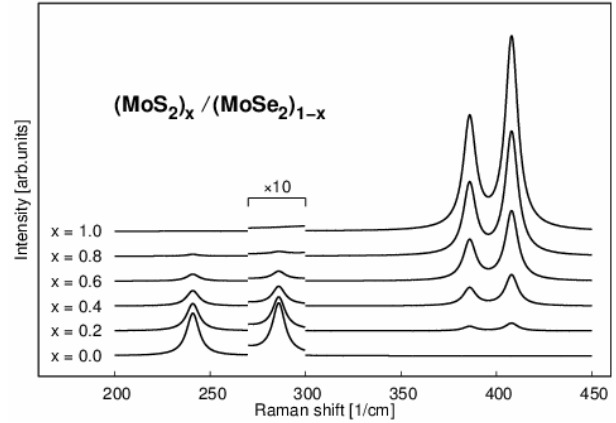
important in one-layer crystal and is not taken into account in theoretical calculations. Indeed, from work [20] (Fig. 2, upper panel) follows that combination tones  $\omega_{LA}(q_K) + \omega_{LA}(-q_K) \approx \omega_{LA}(q_M) + \omega_{LA}(-q_M) \approx 470 \text{ cm}^{-1}$  are full symmetric and have frequency higher than  $\omega_{A_1}$ . Therefore, both vibrations can take part in FR interaction, and, as a result, the fundamental band should be shifted some down to the value  $\omega_{A_1} \approx 404 \text{ cm}^{-1}$  that is observed in experiment. The same shift down should occur for the one-layer fundamental vibration  $\omega_{E_1} = 391.7 \text{ cm}^{-1}$  due to FR with combination tone  $\omega_{LA}(q_K) + \omega_{TA}(-q_K) \approx 420 \text{ cm}^{-1}$ . The experimentally observed its one-layer final position is  $\omega_{E_1} \approx 383 \text{ cm}^{-1}$ . On the other hand, when increasing the layer numbers (to 6...8 layers), properties of this thin crystal become close to those of bulk MoS<sub>2</sub> [9], and the bands discussed above are transformed into a new pair of strong  $A_{1g}$  and  $E_{2g}^1$  ones, and the final position of these bands is ruled by properties of bulk crystal.

One can note that in the Raman spectra of crystals MoS<sub>2</sub> and MoSe<sub>2</sub>, these two fundamental bands  $A_{1g}$  and  $E_{2g}$  (Fig. 1) cannot intermix with one another. The fundamental states, in principle, can be mixed by fourth order anharmonic terms in the potential energy, but both these states should have the same symmetry. It is obvious that direct interaction of  $A_{1g}$  and  $E_{2g}$  layer states are impossible, and they also cannot be intermixed by interlayer interaction, too.

Experimental spectra and theoretical dependences describing their change with the “concentration” of layers in mixed crystals are presented in Figs 1 and 2.



**Fig. 1.** Position and intensities of fundamental bands observed in Raman spectra of bulk crystals MoS<sub>2</sub> and MoSe<sub>2</sub> with real relation of their intensities at the same conditions of experiment.



**Fig. 2.** The change of band intensities in spectra MoS<sub>2</sub> and MoSe<sub>2</sub> as a function of concentration  $x = c_{s_0}$ ,  $1 - x = c_{s_1}$ ,  $c_{s_0} + c_{s_1} = 1$ . Spectra at  $x = 1$  and  $x = 0$  were fitted to experimental ones in Fig. 1. All parameters describing interlayer interaction are taken as high enough,  $\tilde{V}_{(s_1, s_1')}^{(k, p)} = 8 \text{ cm}^{-1}$ .

It should be noted that in MoS<sub>2</sub> bulk crystal, with  $D_{6h}$  point group symmetry, close to considered states  $\omega(A_{1g}) = 412 \text{ cm}^{-1}$  and  $\omega(E_{2g}^1) = 389 \text{ cm}^{-1}$ , the combination tones  $\omega(E_{2g}^1) \pm \omega(E_{2g}^2) = (389 \pm 35) \text{ cm}^{-1}$  are placed which can interact with both bands  $A_{1g}$  and  $E_{2g}$  due to Fermi resonance (FR). The latter is admitted by symmetry relations in  $D_{6h}$  point group,  $E_{2g} \times E_{2g} = A_{1g} + E_{2g}$ . The position and intensities of interacting bands depend on the anharmonic constant  $\Gamma$  responsible for this interaction [18, 19]. As a result of interaction, the fundamental vibration  $\omega(A_{1g}) = 412 \text{ cm}^{-1}$  with the combination tone  $\omega(E_{2g}^1) \pm \omega(E_{2g}^2) = (389 \pm 35) \text{ cm}^{-1}$  the first is some shifted down to the value  $\approx 408 \text{ cm}^{-1}$  (Fig. 3, curve 2). The combination band  $424 \text{ cm}^{-1}$  is also some shifted upper but its intensity is weak and band is broad (Fig. 2, curve 2). Space between fundamental  $\omega(A_{1g})$  and other combination tone  $\omega(E_{2g}^1) - \omega(E_{2g}^2) = 354 \text{ cm}^{-1}$  is wide enough and influence of the last on  $\omega(A_{1g})$  can be neglected.

The fundamental band  $\omega(E_{2g}^1) = 389 \text{ cm}^{-1}$  also can interact with these combination tones  $\omega(E_{2g}^1) \pm \omega(E_{2g}^2) = (389 \pm 35) \text{ cm}^{-1}$  but this interaction is more complicated because around this fundamental band two combination tones are placed at the same distances:  $\omega(E_{2g}^1) + \omega(E_{2g}^2) = 424 \text{ cm}^{-1}$  and  $\omega(E_{2g}^1) - \omega(E_{2g}^2) =$

$= 354 \text{ cm}^{-1}$ . According to the theory of FR in crystals [18, 19], the intensity of scattering (absorption) is described by the renormalized constant  $\Gamma$ , and for each of the studied cases it is given by the following relations: for the first case  $\Gamma \rightarrow \Gamma_+ = \Gamma [1 + n(E_{2g}^2) + n(E_{2g}^1)]$  and for the second one  $\Gamma \rightarrow \Gamma_- = \Gamma [n(E_{2g}^2) - n(E_{2g}^1)]$ , where  $n(E_{2g}^2)$ ,  $n(E_{2g}^1)$  are filling numbers of corresponding phonons. It is obvious that  $\Gamma_+ > \Gamma_-$ , and so the fundamental band of MoS<sub>2</sub>,  $\omega(E_{2g}^1) = 389 \text{ cm}^{-1}$ , should be shifted some below, as a result of two noted FR interactions, to the value  $\omega(E_{2g}^1) = 383 \text{ cm}^{-1}$  (Fig. 3, curve 4).

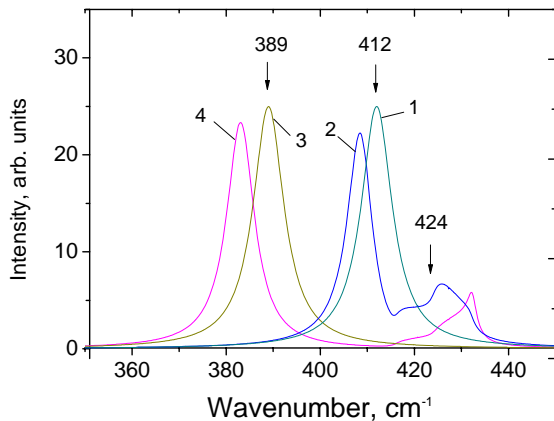
These new states that take part in FR with the fundamental ones  $A_{1g}$  and  $E_{2g}$  will be marked with the index B:  $\omega_B$ ,  $D_{s_A s_B}$ ,  $\Delta_{s_A s_B}$ ,  $D_{s_E s_B}$ ,  $\Delta_{s_E s_B}$ , etc. (see Eqs. (22a, b)). For example, the position of bands for crystal with one type of layer  $s_0$  for vibration of A-type, interacting with B-type vibrations are described by the following relation

$$\omega_{\pm} = \left[ \frac{1}{2} \left\{ (\omega_{s_A}^2 - D_{s_A s_A}) + (\omega_{s_B}^2 - D_{s_B s_B}) \right\} \pm \sqrt{ \left[ (\omega_{s_A}^2 - D_{s_A s_A}) - (\omega_{s_B}^2 - D_{s_B s_B}) \right]^2 + 16\omega^2\gamma^2 + 4D_{s_A s_B} D_{s_B s_A} } \right] \pm \gamma^2 \quad (29)$$

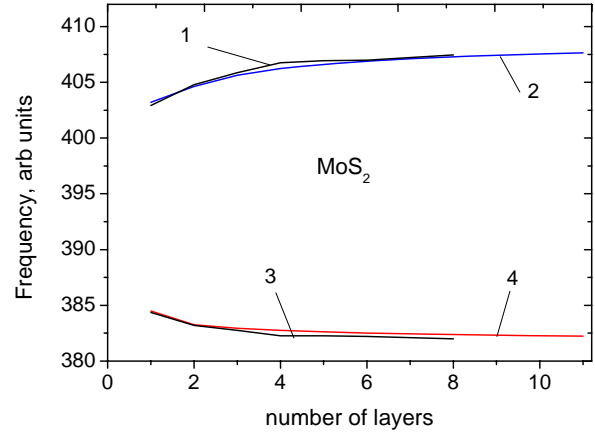
where  $c_{s_0} \rightarrow c_{s_A} = 1$ ,  $c_{s_1} \rightarrow c_{s_B} = 1$ , and instead of Eqs. (22a, b) we have

$$\Delta_{s_j s_{j'}} = (\omega^2 - \omega_{k, s_j}^2) \delta_{s_j s_{j'}} + \omega_{k, s_j} \tilde{V}_{(s_j, s_{j'})}^{(k, p)}, \quad (30a)$$

$$D_{s_j s_{j'}} = \omega_{k, s_j} \tilde{V}_{(s_j, s_{j'})}^{(k, p)}. \quad (30b)$$



**Fig. 3.** Effect of FR interaction with combination tones at the position of fundamental  $\omega_{A_{1g}} = 412 \text{ cm}^{-1}$  and  $\omega_{E_{2g}} = 389 \text{ cm}^{-1}$  bands in bulk MoS<sub>2</sub>.



**Fig. 4.** The change of intra-layer phonon frequencies  $\omega_{A_1} \approx 404 \text{ cm}^{-1}$  and  $\omega_{E_1} \approx 384 \text{ cm}^{-1}$  with increasing the layer numbers and conversion of them into the bulk ones  $\omega(A_{1g}) \approx 408 \text{ cm}^{-1}$  and  $\omega(E_{2g}^1) \approx 383 \text{ cm}^{-1}$ ; curves 1, 3 are experimental, curves 2, 4 are theoretical; parameters:  $2 - \omega(A_{1g})$ ,  $\tilde{V}_0^{(k, p)}(s_0, s_0) = -8 \text{ cm}^{-1}$ ,  $\tilde{V}_0^{(k, p)}(s_0, s_1) = \tilde{V}_0^{(k, p)}(s_1, s_0) = -6 \text{ cm}^{-1}$ ,  $\tilde{V}_0^{(k, p)}(s_1, s_1) = -3 \text{ cm}^{-1}$ ;  $4 - \omega(E_{2g}^1)$ ,  $\tilde{V}_0^{(k, p)}(s_0, s_0) = -5 \text{ cm}^{-1}$ ,  $\tilde{V}_0^{(k, p)}(s_0, s_1) = -4 \text{ cm}^{-1}$ ,  $\tilde{V}_0^{(k, p)}(s_1, s_1) = -2 \text{ cm}^{-1}$ .

Interlayer interaction between different layers is described by the following expression (that will be considered in details elsewhere)

$$\tilde{V}_N^{(k, p)}(s_j, s_{j'}) \approx \tilde{V}_0^{(k, p)}(s_j, s_{j'}) \sum_{n=1}^N \frac{1}{n^{1+\alpha}}, \quad \alpha > 0, \quad (30c)$$

$\tilde{V}_0^{(k, p)}(s_j, s_{j'})$  describes the change of interaction energy between two layers when changing their excitation from  $s_0^j$  state to  $s_0^{j'}$  one; in our case  $\alpha = 0.45$ . It is seen from Eqs. (29) and (30a-c), if interlayer interaction  $\tilde{V}_{(s_j, s_{j'})}^{(k, p)} = 0$ , ( $\gamma \rightarrow 0$ ) frequencies are correspondingly equal (if  $\omega_B < \omega_{s_A}$ ):  $\omega_+ = \omega_{s_A} = \omega_{A_{1g}}$  and  $\omega_- = \omega_B$ . With inclusion of interlayer interaction,  $\tilde{V}_{(s_j, s_{j'})}^{(k, p)} \neq 0$ , intermixing the layer fundamental vibrations occurs, and frequencies  $\omega_+$  and  $\omega_-$  are additionally shifted to some extent into different sides. Fitting dependence described by Eq. (29) to experiment [9] gave the possibility to obtain parameters of interlayer interactions  $\tilde{V}_0^{(k, p)}(s_j, s_{j'})$ , which are given as legend to Fig. 4 and parameter  $\alpha = 0.45$ .

## 5. Conclusion

The change of intensities and position of bands for in-plane  $E_{2g}^1$  and out-of-plane  $A_{1g}$  vibrations as a function of the “concentration” of corresponding type layers was studied. The dependence of internal layer phonon frequencies on interlayer interactions and estimation of interlayer interaction by using the comparison of experimental results and theory was obtained.

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