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LOW-TEMPERATURE ELECTRON SPECTRA OF IMPURITIES IN NAPHTALENE CRYSTALS

This work relates to the study of vibrational structures in the electron spectra of naphthalene crystals with impurities of β- and α-naphthalene fluorine with concentrations of 10^{-4} to 10 wt.% at a temperature at 4.2 K. It is determined that, at low impurity concentrations, the spectra have a doublet structure and consist of narrow quasilines with initial values of ν_{01} = 31322 cm^{-1} and ν_{02} = 31226 cm^{-1}, which are resonance-coincident in the absorption and fluorescence spectra. It is demonstrated that if the impurity concentration increases, the series of narrow quasilines appear in the areas of the 0-0 transitions of the impurity centers of both types together with the doublet structure. A part of these quasilines is polarized predominantly along the b-axis of a naphthalene crystal. The model is proposed for impurity centers, which induce the generation of new spectral bands. This model is based on the interaction of translation-nonequivalent impurity molecules in the elementary lattice cell of a naphthalene crystal. At high impurity concentrations, the resonance-symmetric wide spectral bands appear in the absorption and fluorescence spectra. The analysis of the results obtained is performed with consideration for the Franck–Condon interaction and the Herzberg–Teller interaction.

Keywords: vibrational structure, absorption and fluorescence spectra, β- and α-naphthalene fluorine, impurity center.

1. Introduction

To study the electron-vibrational structure of absorption and fluorescence spectra of impurity centers in crystals, many theoretical and experimental works have been performed. The foundations of the state-of-art quantum-mechanical theory explaining the properties of absorption and fluorescence spectral bands corresponding to impurities in crystals have been presented in various scientific publications [1–3].

Among the experimental works related to this problem, it is important to note numerous experimental studies of the impurity-bearing molecular crystals. Molecular crystals are distinctive by that their spectra, specifically at low temperatures, have well-defined purely electron transitions and a sophisticated electron-vibrational structure. In most cases, the characteristic feature of the absorption and fluorescence spectra of impurity molecular crystals is the presence of two systems of spectral bands, that is, a system of narrow spectral bands and a system of wide structureless spectral bands. The positions, shapes, and intensities of these spectral bands depend considerably on the temperature and the concentration of an impurity.

In a number of works, it was demonstrated that monosubstituted derivatives of naphthalene, which are dissolved in crystalline naphthalene, generate impurity centers of two types represented in the absorption and fluorescence spectra by two identical series of spectral bands [4–7]. The initial spectral bands of these series in the fluorescence spectrum are resonance-coincident with the corresponding bands in the absorption spectrum. The doublet structure of the fluorescence spectrum is caused by that there

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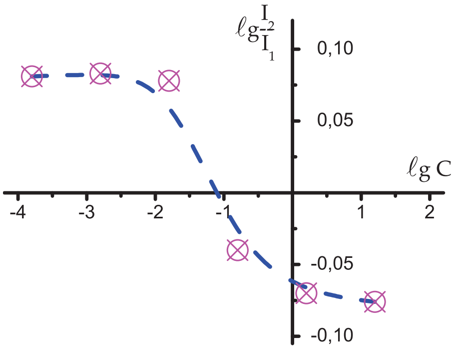

Fig. 1. Dependence of the ratio of impurity centers of types II and I on the impurity content

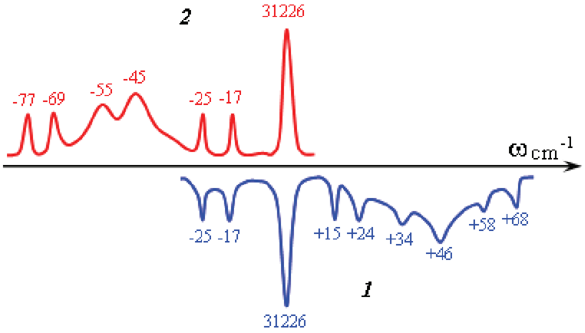

Fig. 2. Schematic representation of the fluorescence (*2*) and absorption (*1*) spectra of β-naphthalene fluorine in naphthalene in the impurity band with $\nu_{02} = 31226$ cm^{-1}

are two different modes of substitution of naphthalene molecules in a crystal lattice cell with impurity molecules [8]. It was also demonstrated that the wide structureless spectral bands and some narrow quasilines appear in the spectra, additionally to the doublet structure, if the impurity concentration increases.

This paper presents the experimental results allowing the properties of the absorption and fluorescence spectra of both types to be determined. For this purpose, an integrated study was performed for explaining the electron-vibrational structure of the absorption and fluorescence spectra of impurity naphthalene crystals containing impurities of β- and α-naphthalene fluorine.

2. Experimental Results

The absorption and fluorescence spectra were recorded by a spectrometer DFS-13 (inverse linear dispersion 4 Å/mm) and a spectrophotometer MPF-4 Hitachi (inverse linear dispersion 3 Å/mm). For measurements at a temperature of 4.2 K, a helium cryostat was used. The sample substances were purified by the zone melting. The impurity concentration was varied in the range from 10^{-4} to 10 wt%.

The results of the analysis of the absorption and fluorescence spectra in a wide range of concentrations of β-naphthalene fluorine in naphthalene allow the characteristic features of the spectra to be determined. These characteristic features are discussed below.

1. In the range of low impurity concentrations from 10^{-4} to 10^{-1} wt%, the absorption spectra contain two initial spectral bands with the frequencies $\nu_{01} = 31322$ cm^{-1} (I – impurity center) and $\nu_{02} = 31226$ cm^{-1} (II – impurity center), which are resonance-coincided with the corresponding spectral bands in the fluorescence spectra.

2. The results of the analysis of the relative intensities of spectral bands with ν_{01} and ν_{02} in the absorption spectra demonstrate that, in the range of impurity concentrations 10^{-4}–10^{-2} wt%, the number of type II impurity centers exceeds the number of type I impurity centers. If the impurity concentration increases, the relative intensities of the spectral bands considerably change. So, this feature may be interpreted as the indication of the preferential growth of type I impurity centers (Fig. 1).

3. Together with the aforesaid changes of the relative intensities of spectral bands with ν_{01} and ν_{02} (Fig. 1) in the absorption spectra, at the impurity concentration of 0.1 to 10 wt%, the series of accompanying blurred narrow spectral bands appear within the 0-0 transition areas of the impurity centers of both types. Thus, on either side of the 0-0 spectral band corresponding to the type II impurity center, the doublets of narrow spectral bands with the same intensity appear, that is, the doublet of bands on the long-wave side, located at distances of 17 cm^{-1} and 25 cm^{-1}, which are resonance-coincident with the corresponding bands in the fluorescence spectra, and the doublet of bands located at distances of 15 cm^{-1} and 24 cm^{-1} on the short-wave side (Fig. 2). The mentioned accompanying bands appear also in the fluorescence spectrum near the spectral bands, which are characterized by the combination of a purely electron transition with the most intensive intramolecular vibrations at 523, 771, and 1382 cm^{-1}.

4. In the absorption and fluorescence spectra of the impurity centers of both types, the wide blurred spectral bands with a half-width of about 50 cm^{-1} appear together with intense 0-0 quasilines. Against the background of these spectral bands, the peaks on both sides of the 0-0 transitions, at distances of 46 cm^{-1} from the transitions, and a number of less intense spectral bands are located (Fig. 2).

5. As the impurity concentration increases up to 5×10^{-2}–0.5 wt%, the intensity of the fluorescence spectra of the type I impurity centers significantly decreases as compared with the type II impurity centers, notwithstanding that the results of the analysis of the absorption spectra at the same impurity concentration demonstrate that the number of the type I impurity centers exceeds the number of the type II impurity centers.

Similar results were obtained for impurities of α-naphthalene fluorine in naphthalene. The impurity molecules are also inserted into crystal lattice cells according to two modes. Two series of identical spectral bands in the absorption and fluorescence spectra correspond to these two modes. But the intensity of the 0-0 spectral band of the long-wave series with $\nu_{02} = 31370$ cm^{-1} in the absorption spectrum considerably exceeds the intensity of the identical band of the short-wave series with $\nu_{01} = 31401$ cm^{-1} (Fig. 3). At the impurity concentration of about 1 percent, two narrow spectral bands appear on the long-wave side from the 0-0 spectral band of the type II impurity center, at distances of 13 cm^{-1} and 20 cm^{-1} from the 0-0 spectral band, and two weak spectral bands polarized along the b-axis of the naphthalene crystal appear on the short-wave side. Additionally, a wide structureless spectral band about 40 cm^{-1} in width, having three peaks, appears. The maximum point of the most intense peak is positioned at a distance of 50 cm^{-1} from the band with $\nu_{02} = 31370$ cm^{-1}.

In the absorption spectra of such impurities as α-naphthalene fluorine and β-naphthalene fluorine in naphthalene, near the a-band of the Davydov doublet, on the long-wave side, at identical distances 12 cm^{-1}, a narrow spectral band polarized along the b-axis of the naphthalene crystal appears. This spectral band is similar to the new spectral bands which have been observed in naphthalene crystals with impurities of heterocyclic compounds and are associated with electron transitions in the naphthalene molecules activated by impurity molecules [9].

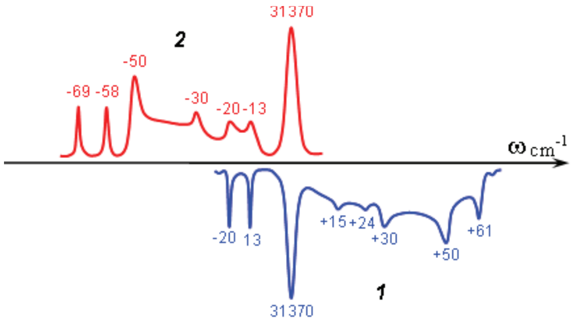

Fig. 3. Schematic representation of the fluorescence (*2*) and absorption (*1*) spectra of α-naphthalene fluorine in naphthalene in the impurity band with $\nu_{02} = 31370$ cm^{-1}

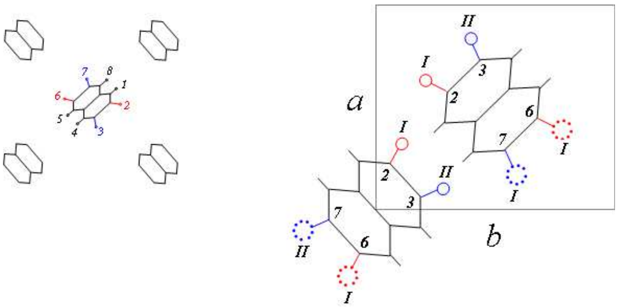

Fig. 4. Variants of the generation of translation-nonequivalent pairs of β-naphthalene fluorine in the lattice of a naphthalene crystal

3. Discussion of Results

In order to determine the origin of the narrow spectral lines located near the 0-0 spectral bands of impurity centers, the absorption spectra in polarized light were obtained for β-naphthalene fluorine in naphthalene. On either side of the band with $\nu_{02} = 31226$ cm^{-1}, two narrow spectral bands of the same intensity are asymmetrically located. The outer lines are polarized predominantly along the b-axis of the naphthalene crystal, and the inner lines are weakly polarized. As naphthalene monocrystals are formed with a sophisticated a-b plane, the generation of pairs of translatorily nonequivalent impurity molecules is possible at certain impurity concentrations.

Figure 4 illustrates the possible variants of the generation of pairs of translatorily nonequivalent impurity molecules of β-naphthalene fluorine in the lattice of a naphthalene crystal. If the naphthalene molecule to be substituted is in position 2 or 6 in the naphthalene crystal, a single impurity molecule, when substituting the naphthalene molecule, generates a type I impurity center. If the naphthalene molecule to be substituted is in position 3 or 7, a type II impurity center is generated. As is clear from Fig. 4, for each impurity center, there are two variants of positioning impurity molecules in a single crystal lattice cell (e.g., when the molecules to be substituted are in positions 2 and 2 or 2 and 6). In this case, as a result of the resonance interaction, two energy levels are formed in each pair of molecules. These energy levels are located symmetrically on both sides of the monomer energy level: $\varepsilon_{2,6} = \pm M_{2,6}$. As was mentioned above (Fig. 2), the absorption spectrum contains a long-wave doublet (located at distances of 17 cm^{-1} and 25 cm^{-1} of the 0-0 spectral band) and a short-wave doublet (located at distances of 15 cm^{-1} and 24 cm^{-1} of the 0-0 spectral band). The spectral bands remoted by 25 cm^{-1} and 24 cm^{-1} are predominantly polarized along the b-axis of the naphthalene crystal. Let us assume that the probabilities of the generation of pairs of molecules 2, 2 and 2, 6 are equal. Then the intensities of these spectral bands should also be equal, as is confirmed experimentally. As the spectral bands of the doublet 17 cm^{-1} and 25 cm^{-1} are resonance-coincident with the identical spectral bands in the fluorescence spectrum, each component of the doublet corresponds to a certain type of molecule pairs. Otherwise, the ultraviolet component should not appear in the fluorescence spectrum. Similar doublets are present in the case of α-naphthalene fluorine.

Impurity molecules of β-naphthalene fluorine, when substituting molecules of naphthalene in the impurity crystal lattice, increase the free energy of the impurity crystal by ΔF. The free energy of the crystal consists of three components: $F = U + E^{\text{vibr.}} -$ TS, where U is the energy of interaction of particles in the equilibrium state, $E^{\text{vibr.}}$ is the vibrational energy of the crystal lattice, and TS is the crystalline entropy [10].

The changes of the free energy of a naphthalene crystal when a naphthalene molecule is substituted with a β-naphthalene fluorine molecule according to the first mode and the second mode can be expressed as follows:

$$\Delta F_1 = \Delta U_1 + \Delta E_1^{\text{vibr.}} - T\Delta S_1,$$

$$\Delta F_2 = \Delta U_2 + \Delta E_2^{\text{vibr.}} - T\Delta S_2.$$

The second and third terms of the expressions for ΔF_1 and ΔF_2 depend on the thermal properties of the same β- naphthalene fluorine impurity, so the difference of these terms is determined as follows:

$$\Delta F_1 - \Delta F_2 = \Delta U_1 - \Delta U_2.$$

If the distribution of β-naphthalene fluoride molecules in naphthalene between type I impurity centers and type II impurity centers is specified as the ratio of the number n_2 of the type II impurity centers to the number n_1 of the type I impurity centers, then, according to the Boltzmann distribution law, $n_1 \sim \exp(\Delta U_1/kT)$, $n_2 \sim \exp(\Delta U_2/kT)$, and $m = n_2/n_1 = \exp((\Delta U_2 - \Delta U_1)/kT)$.

It is also possible (Fig. 1) to determine the absorption intensity for the type II impurity center relative to the absorption intensity for the type I impurity center in the range of impurity concentrations from 10^{-4} to 10^{-1} wtthis relative intensity is about 1.2. In this case, the difference $\Delta U_2 - \Delta U_1$ at room temperature is about 40 cm^{-1}. Therefore, the difference between the minima of the potential curves for the type I impurity center and the type II impurity center in the lowest energy state is 40 cm^{-1}. The results of the analysis of the fluorescence spectra at the same impurity concentrations demonstrate that the ratio of the fluorescence intensity of the type II impurity center to that of the type I impurity center also exceeds 1.0 and is constant in the indicated impurity concentration range. This implies that there is no energy migration between the impurity centers, i.e., the impurity centers radiate energy independently of one another.

If the impurity concentration exceeds 0.2%, the ratio of intensities $I_2/I_1 = 0.83$ corresponds to the difference $\Delta U_1 - \Delta U_2 \approx 35$ cm^{-1}. This value is close to the aforesaid value of 40 cm^{-1}. So, the number of the type I impurity centers exceeds the number of the type II impurity centers. On the contrary, in the fluorescence spectra, the fluorescence intensity of the type I impurity centers decreases. So, there is the migration of the absorbed energy due to the generation of various combinations of impurity molecules.

Hereinbefore, the case of the generation of resonance pairs from impurity molecules, which pertain to the same impurity center (2, 2 or 2, 6) has been

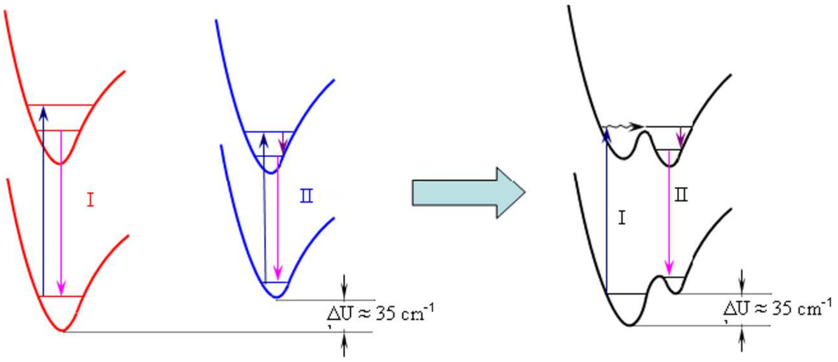

Fig. 5. Configuration curves for the ground and excited states of pairing impurity centers

discussed. With the same probability, impurity centers can be generated in the case of the interaction of pairs of molecules 2, 3 or 2, 7. So, the model of a pairing impurity center consisting of impurity molecules pertaining to different impurity centers can be represented by potential curves (Fig. 5). In this case, the total energy absorbed by the type I impurity center is completely transferred to a type II impurity center. As the impurity concentration increases, the number of pairing impurity centers increases at the expense of single impurity centers. Therefore, the number of single impurity centers decreases as compared with the pairing impurity centers, and the intensity of fluorescence of the single impurity centers also considerably decreases, as is evident from the experimental results.

The analysis of the electron-vibrational structure of impurity center spectra was performed by studying the interaction of impurity molecules with the lattice phonons of the crystal dissolver [10]. In this case, the wide spectral bands accompanying the lines of 0-0 transitions in the absorption and fluorescence spectra of the impurity centers of both types can be generated due to the electron-phonon interaction of the impurity molecules with the lattice phonons of the naphthalene crystal. The spectral band corresponding to the 0-0 transition in the impurity center is a phononless spectral line, and the wide bands on the long-wave and short-wave sides of the phononless spectral line in the absorption and fluorescence spectra are phonon wings. The shape and the intensity of a phonon wing depend on three parameters a, W, and $M(R)$, where a is the shift of the minima of the multidimensional energy surface, W is the change in the shape of the multidimensional energy surface under the electron excitation of the impurity center, and $M(R)$ is the matrix element of the operator describing the electron interaction of an impurity molecule with light. The first two parameters are characteristic of the Franck–Condon interaction, and the third parameter is characteristic of the Herzberg–Teller interaction. If the phonon wings are caused by the Franck–Condon interaction, these phonon wings in the conjugate absorption spectrum and fluorescence spectrum are asymmetrically located relative to the spectral band of the 0-0 transition of the impurity center. If the 0-0 spectral bands of impurity centers are considered as phononless lines, the results of the analysis of the absorption and fluorescence spectra demonstrate that the wide phonon wings, appearing as wide bands with a half-width of about 50 cm^{-1}, are present in the conjugate absorption spectrum and the fluorescence spectrum of the impurity centers of both types. Against the background of these bands, the peaks of narrower lines are distinctly generated. As is shown in Fig. 2, these peaks are asymmetrically located virtually at equal distances of 45 cm^{-1} from the corresponding 0-0 spectral band. Additionally, on both sides of these bands, the blurred weaker bands are present. Some of these bands have asymmetric counterparts.

In the case of the impurity of α-naphthalene fluorine in naphthalene, there also is the asymmetry of phonon wings relative to the type II impurity center with $\nu_{02} = 31370$ cm^{-1}. The main peaks of these wide phonon wings are located at an exact distance of $+50$ cm^{-1} from the 0-0 spectral band in the absorption spectrum and –50 cm^{-1} from the 0-0 spectral band in the fluorescence spectrum. As is shown in Fig. 3, there is a discontinuity ($\sim$40 cm^{-1}) between the long-wave edge of the phonon wing in the absorption spectrum and the short-wave edge of the phonon wing in the fluorescence spectrum. Additionally, the shapes of spectral bands in the absorption spectrum and the fluorescence spectrum are slightly different. So, the difference of the shapes of conjugate spectral bands in the absorption spectrum and the fluorescence spectrum, and the asymmetry of some frequencies in these spectra are indicative of the effect of the shape of the multidimensional energy surface under the electron excitation of the impurity center on the generation of phonon wings.

In order to determine whether the wide structureless bands are phonon wings at the corresponding electron-vibrational transitions, it is necessary to study and to analyze the effect of the temperature on the shapes and the relative intensities of narrow the spectral lines of purely electron transitions and wide asymmetric spectral lines in absorption and fluorescence spectra.

4. Conclusions

1. It is demonstrated that, at higher concentrations of β-naphthalene fluorine impurity in naphthalene of 1^{-1}–10 wt%, the absorption and fluorescence spectra contain additional spectral bands near the 0-0 bands of impurity centers of both types. These additional spectral bands are caused by the generation of pairing impurity centers from the impurity molecules located at translation-nonequivalent points in the same crystal lattice cell.

2. The model of a pairing impurity center generated from impurity molecules pertaining to different impurity centers is proposed. This model provides the possibility to explain the decrease of the intensity of the impurity centers of one (band $\nu_{01} = 31322$ cm^{-1}) of two types in the fluorescence spectrum.

3. It is determined that the asymmetric phonon wings, as wide spectral bands, appear near each band in the conjugate absorption spectrum and fluorescence spectrum of the impurity centers.

4. It is found that, in the range of the beta naphthalene fluorine concentration in naphthalene from 5×10^{-2} percent to 0.5 percent, the coefficient of distribution of impurities between type I impurity centers and type II impurity centers changes from 1.2 to 0.83.

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1. S.I. Pekar, *Research in Electron Theory of Crystals* (United States Atomic Energy Commission, Washington, DC, 1963).
2. A.S. Davydov, ZhETPh **24**, 197 (1953).
3. M.A. Krivoglaz and S.I. Pekar, Trudy Inst. Fiz. AN UkrSSR **4**, 37 (1953).
4. E.V. Shpol'skii, Uspekhi Fiz. Nauk **71**, 215 (1960).
5. M.T. Shpak, *Experimental Studies of Luminescense of Molecular Crystals*, Doctoral Dissertation (Kiev, 1964) (in Russian).
6. I.S. Osad'ko, R.I. Personov, and E.V. Shpol'skii, Izv. AN SSSR, Ser. Fiz. **37**, 540 (1973).
7. P.C. Freeman and N.P. Paras, Chem. Phys. Lett. **72**, 285 (1980).
8. N.D. Kurmei, G.V. KLishevich, V.I. Mel'nik, A.G. Tereshchenko, D.I. Zloba, and D. Shcherban, Zh. Prikl. Spektr. **80**, 532 (2013).
9. N.I. Ostapenko, V.I. Sugakov, and M.T. Shpak, *Spectroscopy of Defects in Molecular Crystals* (Naukova Dumka, Kiev, 1988) (in Russian).
10. A.I. Kitaigorodskii, *Molecular Crystals* (Nauka, Moscow, 1971) (in Russian).

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НИЗЬКОТЕМПЕРАТУРНІ ЕЛЕКТРОННІ СПЕКТРИ ДОМІШОК У КРИСТАЛАХ НАФТАЛІНУ

Резюме

Робота присвячена дослідженню коливальної структури в електронних спектрах кристалів нафталіну з домішкою β- та α-фторнафталіну в інтервалі концентрацій від 10^{-4} до 10 вагових процентів при $T = 4{,}2$ К. Встановлено, що при низьких концентраціях домішки спектри являють собою вузькі квазілінійчаті серії смуг, що мають дублетний характер з початковими значеннями: $\nu_{01} = 31322$ $\mathrm{см}^{-1}$ і $\nu_{02} = 31226$ $\mathrm{см}^{-1}$, які резонансно збігаються в спектрах поглинання та флуоресценції. Показано, що з ростом концентрації домішки поряд з дублетною структурою в області 0-0 переходів обох центрів виникає ряд вузьких квазіліній, частина з яких поляризована переважно за b-напрямком у кристалі нафталіну. Запропоновано модель центрів, відповідальних за появу нових смуг, яка ґрунтується на врахуванні взаємодії трансляційно нееквівалентних молекул домішки в елементарній комірці кристала нафталіну. При великих концентраціях домішки спостерігаються резонансно симетричні широкі смуги, в спектрах поглинання і флуоресценції. Аналіз отриманих результатів проводиться з урахуванням франк–кондонівської та герцберг–теллерівської взаємодій.