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OPTICAL SPECTRUM AND MAGNETO-OPTICAL PROPERTIES OF EXCITONS

K.V.GROSS

A complex structure consisting of narrow strong absorption lines is observed at the edge of fundamental absorption of a number of crystals at low temperatures. A structure of such kind has already been known well in crystals of alkali halides since the time of Hilsch and Pohl[1]. The recent works have established that the structure of the fundamental absorption edge is some common phenomenon, detected in a number of crystals:x) Cu_2O, CdS, CdSe, ZnS, HgJ_2, PbJ_2, CuCl, CuBr, CuJ, BaO and others.

The large absorption coefficient in structure lines allows us to refer them to the crystal lattice. This very fact, together with the disposition of the lines at the very edge of fundamental absorption give us grounds to connect the linear structure with formation of excitons, theoretically forecast by Frenkel[2].xx)

I shall mainly dwell on the investigations of my laboratory in Leningrad carried on with the active participation of N.A. Karryev, B.P.Zanarčenja, A.A.Kaplyansky, B.S.Razbyrin, B.V.Novyikov, V.B.Sobolev, M.A.Jakobson and others.

The most interesting and clear results have been obtained on the cuprous oxide crystal where, at the absorption edge, two series of narrow lines, "yellow" and "green", can be observed (Fig.I). The frequencies of these lines, converging to the series limits, well satisfy the hydrogen-like relation of the kind:

$$\nu_n = \nu_\infty - \frac{R_{ex}}{n^2} \qquad \text{.....} \quad (I)$$

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x) However, it must be noted, that in some crystals, such as: V_2O_5, MoO_3, As_2S_3, Bi_2O_3, TiO_2 and some others the structure at the absorption edge has not been found.

xx) However, one should always bear in mind that some narrow absorption lines may be connected with impurities centres and de

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n = [illegible] ... for "yellow" series

n = [illegible] for "green" series

where [illegible] - the frequency of the series limit (the photodissociation of exciton), n - quantum number, R_{ex} - the Rydberg constant for the exciton, connected with the Rydberg constant R by the relation:

$$R_{ex} = \frac{R \, \mu^* / m}{n_o^4}$$

where n_o is the index of refraction, m is the electron mass in vacuum, μ^* is the reduced effective mass of the exciton,

$$\frac{1}{\mu^*} = \frac{1}{\mu_e^*} + \frac{1}{\mu_h^*}$$

where μ_e^* and μ_h^* are the effective masses of the electron and the hole.

The hydrogen-like series in cuprous oxide points to existance of Mott excitons in the crystal.

Considering the hydrogen-like model of the Mott exciton /3/ one can calculate the exciton diameter in the cuprous oxide crystal with the formula:

$$d_{ex} = 2 \, \hbar^2 / \mu e^2 \cdot n_o^2 \, n^2 \quad \ldots\ldots\ldots \quad (2)$$

where n_o is the index of refraction (n_o = 2,5 for Cu_2O), μ is the reduced effective mass of the exciton.

Defining μ from the exciton series ($\mu \cong 0,25$ m), we obtain from the formula (2) for lowest and highest experimental values of n the sizes of the exciton diameters:

n = 2 $\qquad d_{2\,ex} \cong 100$ Å

n = 10 $\qquad d_{10\,ex} \cong 500$ Å

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Hence, it is evident that the exciton diameters for high excitation states (great quantum numbers) are extremely ~~great~~ large.

Naturally, mistrust and doubt may arise as to whether there can really exist in crystals quasi-atoms-excitons consisting of electron and hole of such ~~great~~ large size. Perhaps this idea of exciton is a result of a wrong interpretation of experimental fact - the existence in the Cu_2O crystal spectrum of a ten-member series. However, we must necessarily come to the conclusion that such great excitons do exist in crystals. This is pointed at by two independent phenomena which we were able to observe in the exciton spectrum - the Stark effect and the Zeeman effect.

Zamarčenja, Rejnov and I were able to observe /4/ the Stark effect on the members of the exciton series even in a weak electric field $E = 5$ kv/cm. That is possible only when the exciton sizes are very ~~great~~ large. It is further possible to observe the phenomenon of the ionization (dissociation) of exciton by weak electric field. Beginning with the field ~~tension~~ strength $E = 6$ kv/cm the high members of the series gradually disappear being covered by the fundamental absorption edge shifting on the exciton series (Fig.2). As the field increases the absorption edge covers more and more series members so that when the field $E = 30$ kv/cm, the whole exciton yellow series disappears. The exciton dissociates under the influence of the field which tears off the electron from the hole. The tearing off the electrons by the electric field is also observed in atoms though the field then is very strong $E = 1000$ kv/cm. The fact that the same phenomenon is observed in excitons with fields a hundred times less points to the large size of the exciton's orbits.

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Further, our research work with Zahareenja has shown /5/ that the members of the exciton series in Cu_2O do not display an ordinary paramagnetic Zeeman effect proportional to the magnetic field H but a diamagnetic one proportional to the square of the magnetic field. Under the influence of the magnetic field there takes place a shift of the splitted exciton lines to the violet part of the spectrum towards the series limit (Fig.3). The shift is greater the higher is the quantum number n of series member and increases with the increase of the magnetic field. Investigations have shown /5/ that the shift is proportional to H^2 and n^4.

These experimental results are in full agreement with the theory of diamagnetic quadratic Zeeman effect according to which diamagnetic shift is proportional to the square of the electron orbit radius and, therefore, to quantum number in the fourth power /6/.

$$\Delta W = \frac{e^2}{8\,me^2} \overline{(x^2 + y^2)} \quad H^2 \ldots\ldots\ldots\ldots (3)$$

Agreement between experiment and theory shows that the observed shift of the series members of exciton in a magnetic field is due to the diamagnetism of exciton. The diamagnetic shift in the Zeeman effect is very great as can readily be observed with the series member having the quantum number n = 3, while in atomic spectra such a shift is observed /7/ on very high series members (n = 30) only. This shows that the exciton diamagnetism is very great; that, in its turn, is a consequence of very large exciton orbits.*)

The diamagnetic shift in the exciton spectrum (formula /3/) allows to determine the exciton radius. The shift for series

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member $n = 5$ measured experimentally is $1,8\ cm^{-1}$. This value determines the exciton diameter according to formula (3). When $H = 20000$ oersted, the exciton diameter becomes $d_{5\ ex} = 400$ Å. The size of the diameter for the same excited state of the exciton calculated (formula /2/) from the Mott exciton model was found to be $d_{5\ ex} = 500$ Å. The agreement between the calculated values is good enough considering the approximate manner of calculation.

Thus, the study of Zeeman effect independently of the Stark effect and the series relations (formula /1/ and /2/), also point to the extremely great dimensions of the exciton in cuprous oxide crystal[x/].

A more thorough study of the Zeeman effect in the exciton spectrum leads to the conclusion[8/] that an ordinary paramagnetic Zeeman effect observed in free atoms is fully absent or rather small in the series members ($n = 3,4,5,6$) of the exciton in Cu_2O crystals. The splitting of the series members is caused by the diamagnetic effect only. This conclusion follows

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x/ While Zahardenja and I were investigating the exciton spectrum in cuprous oxide there arose of course such a question as whether very thin Cu_2O plates can hold such large excitons.

If the Cu_2O plates are thin enough, some of the large excitons especially those which get excited near the surface, cannot be formed and cannot exist in plates. This phenomenon must manifest the disappearance of these lines at the exciton series limit which are connected with the excitation of very large excitons. Perhaps, this is why in the experiments of Zahardenja and myself in thin plates the highest members of the exciton series seem to be weakened near the very limit of the series.

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from a number of observations and from the experimentally established fact that the picture of magnetic splitting is completely or almost completely identical in π and σ components. (Fig.4). This is not observed in Zeeman effect in free atomic systems.

The value of magnetic splitting $\Delta\nu$ of a normal Zeeman triplet in the exciton spectrum must be proportional to $(\mu_e^* - \mu_h^*)$ - the difference between the effective masses of electron and hole in the crystal /9/. The magnetic splitting $\Delta\nu$ may be equal to 0, i.e. the linear Zeeman effect may be absent only when $\mu_e^* = \mu_h^*$. Thus it follows that in a cuprous oxide crystal there exists an exciton of the quasipositronium type with equal or almost equal masses of electron and hole.

This conclusion based on the absence of ordinary paramagnetic Zeeman effect in the series members in Cu_2O is at the same time a proof that the hydrogen-like series of narrow lines in Cu_2O crystal is really due to the exciton and not to some kind of impurity centres or defects in the Cu_2O lattice.. Were the series connected with such centres and not with excitons, the ordinary linear Zeeman effect would have to be observed on the series lines. However this is not observed.

The study of the magnetic field action upon the cuprous oxide exciton spectrum has brought Zaharčenja and myself to one more rather interesting phenomenon /10/. We have discovered that near the series limit, where the diamagnetic shift is comparable with the distance between the neighbouring series members, there appears a spectrum consisting of almost equidis-

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tant lines. The distance between the lines when H = 30000 oersted is about 2 cm^{-1}. Gradually weakening and becoming irregular this linear spectrum extends beyond the series limit where in the absence of a magnetic field a continuous spectrum corresponding to the exciton dissociation is observed. Besides, beyond the exciton series limit on the background of the continuous spectrum there appear in the magnetic field almost equidistant diffuse absorption maxima (Fig.5). When the field H = 30000 oersted, the distance between the absorption maxima is about 7 cm^{-1}. These maxima are superposed by hardly distinguished lines in a way of some kind of fine structure. Thus in a magnetic field the continuous spectrum beyond the exciton series limit is no longer continuous, but reveals two phenomena: 1) absorption maxima beyond the series limit and 2) a fine structure on them. The further the absorption maxima from the series limit (when H = 0) the weaker their intensity and they gradually melt into the continuous absorption background. At magnetic field being equal to H = 30000 oersted we could observe up to ten such maxima.

The described picture of an exciton spectrum in a magnetic field is not to be interpreted as a strong diamagnetic shift of highest series members. The approximate equidistance of absorption maxima beyond the series limit does not correspond to the H^2 law of diamagnetic shift, but the distance between the maxima is proportional to the magnetic field H.

This makes us suppose that here we have to do with a NEW phenomenon of the appearance of diamagnetic levels of exciton

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carrier moving in the magnetic field in accordance with Landau theory /II/ and observed in cyclotron resonance experiments. However, for excitons this phenomenon must have specific outlines. The electron and hole in the exciton are not free; they are bound by coulomb forces. The coulomb forces are strong for the low states of the exciton and predominant as compared with Lorens forces arising from a magnetic field H. On the contrary the coulomb forces are weak at the highest excited states. The magnetic forces are predominant here determining the regularities near the series limit and call forth the equidistant maxima in the exciton spectrum.

Owing to the magnetic field there can exist some nondissociated states of the exciton beyond the series limit. The magnetic field does not let the electron tear off from the hole, i.e. dissociate the exciton and on the contrary keeps the electron and hole in the stable discrete states.

The general picture of continuous absorption with diffuse maxima beyond the exciton series limit (without fine structure) given above is well explained by the Landau /II/ level scheme. It needs no coulomb interaction for its interpretation and might be also observed on free electrons and holes not bounded into an exciton. On the contrary the appearance of discrete lines in the form of some fine structure on these diffuse absorption maxima is called forth by the presence of the coulomb field between electrons and holes even though a weak one at long distances between electron and hole. The appearance of discrete fine structure is typical namely for the bound state of electron and hole, i.e. typical for an exciton.

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The theoretical study of the exciton energy spectrum in a magnetic field made by prof. P.P.Pavinsky, confirms these considerations.

The Shrödinger equation for the motion of hole and electron of the exciton in a field of coulomb forces and a magnetic field H (directed along Z axis) may be written as follows:

$$\left[-\frac{h^2}{2\mu^*}\Delta + \frac{e^2 H^2}{8\mu^* c^2}(x^2+y^2) - \frac{e^2}{\varepsilon r} \right] \Psi = E\Psi \quad \ldots(4)$$

where μ^* is the reduced effective exciton mass, $\varepsilon = n_0^2$ - is the optical dielectric constant. In the equation a member is missing that characterized the paramagnetism of an exciton. As the effective masses of electron and hole in a cuprous oxide crystal are approximately equal $\mu_e^* \simeq \mu_h^*$, this member of the equation (4) is small and may not be taken into account. Weak magnetic effects bound with the shift of the centre of gravity of the exciton are also disregarded.

A mathematical analysis of the solutions of the equation (4) shows that the energy distance ΔE between the absorption maxima beyond the series limit, equals $\Delta E = h\Omega$

where $\Omega = \frac{eH}{\mu^* c}$ ..... - cyclotron frequency, corresponding to the magnetic field H. When H = 39000 oersted and the reduced effective mass $\mu^* = 0{,}25\ m_0$, the calculated value of Ω becomes $\Omega_{calc} = 11\ cm^{-1}$, while the experimental value $\Omega_{exp} = 7\ cm^{-1}$. The difference between these values may be connected with some inaccuracy of the experiment or, possibly, with the dependence of the effective exci[illegible] the magnetic field.

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The frequency Ω, found from the exciton spectrum in a magnetic field is equal to the sum[x] of cyclotron frequencies Ω_e and Ω_h of electron and hole forming the exciton.

$$\Omega = (\Omega_e + \Omega_h); \quad \Omega_e = \frac{eH}{\mu_e^* c}; \quad \Omega_h = \frac{eH}{\mu_h^* c}$$

Ω may be called "the cyclotron frequency of the exciton" as it might have appeared in the absorption of a low-frequency electromagnetic radiation in cyclotron resonance experiments.

It seems to us that the phenomena we have observed - the equidistant structure beyond the exciton series limit of Cu_2O in a magnetic field is by its very nature similar to oscillatory magneto absorption effect observed by Zwerdling and Lax[12] in germanium as well as by Burstein and Piccus[13] in InSb.

Now I should like to return to the problem of exciton sizes in crystals. Besides excitons of large radii there may also exist excitons of small radii in the crystal lattice. Zakarčenja, Razbyrin and I have observed in the spectra of the crystals of cadmium sulfide groups of lines at the edge of fundamental absorption which show an ordinary Zeeman splitting in the magnetic field and do not reveal any diamagnetic shift (Fig.6 and 7). In other words, their Zeeman effect, as it is, differs

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x/ Theoretically it has not been quite cleared up whether the frequency of Ω should be equal to a sum or a halfsum of the cyclotron frequencies Ω_e and Ω_h.

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little from the phenomena observed in free atoms and ions or, for example, in rare earth crystals. It shows that the electron excitation radii here are not large and, probably, do not pass the limit of the elementary crystal cell.

Excitons in crystals can differ not only in size but in mutual spin orientation of electron and hole. That leads to two different kinds of excitons: para-exciton and orto-exciton having different physical properties.

Under the influence of light there may arise in the crystal only para-excitons. Orto-excitons may appear under the action of light waves only in case of some simultaneous disturbing influence which may cause the turn-over of the spins in the exciton. Such a disturbing action at formation of orto-exciton may call forth, for example an electron lattice defect or a paramagnetic ion as well.

The "life-time" of an orto-exciton in a crystal must be substantially longer than of para-exciton, as its annihilation is less probable. The Zeeman effect of the ortho-exciton must differ from the Zeeman effect of para-exciton.

The energy difference between the levels of para- and orto-excitons for excitons of large radii is very little (as for a para- and ortho-positronium). It can be considerably greater only for excitons of a small radii because of the interaction between the electron of the exciton with other electrons of the ion in the lattice, near which the exciton was created. As it is revealed with a helium atom, the levels of an ortho-exciton energetically are bellow to be lower than the levels of a para-exciton. Thus, the absorption (excitation) spectrum of an ortho-exciton, which is to be very weak,

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as well as its emission (luminescence) spectrum at its annihilation must be shifted to the long-wave side from the para-exciton spectrum.

It seems to be possible that the so-called edge emission observed in the luminescence of a number of crystals, is connected with the formation and annihilation of ortho-excitons.

Lately there appeared some theoretical works by Tabuti[14] and Trlifaj[15] studying some aspects of para- and ortho-excitons.

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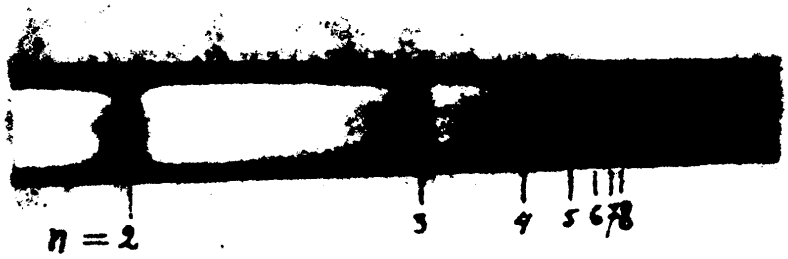

Fig 1

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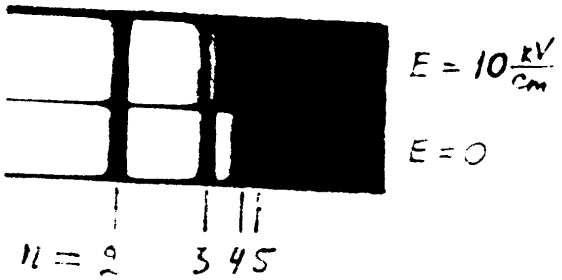

Fig 2

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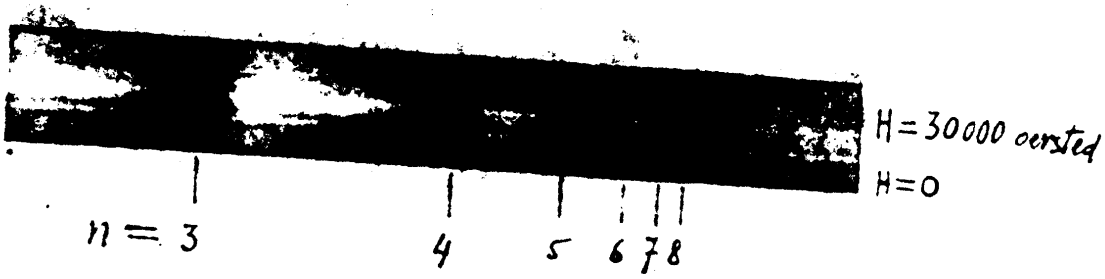

Fig 3

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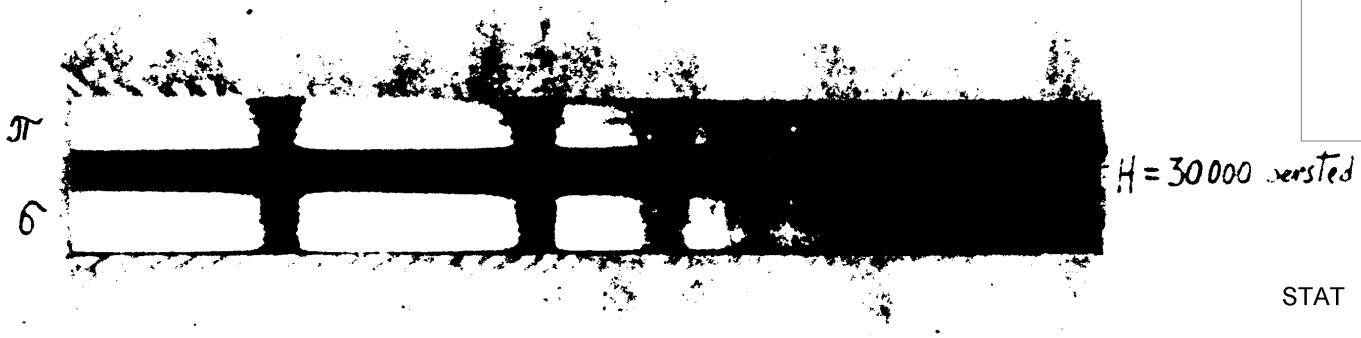

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Fig 4

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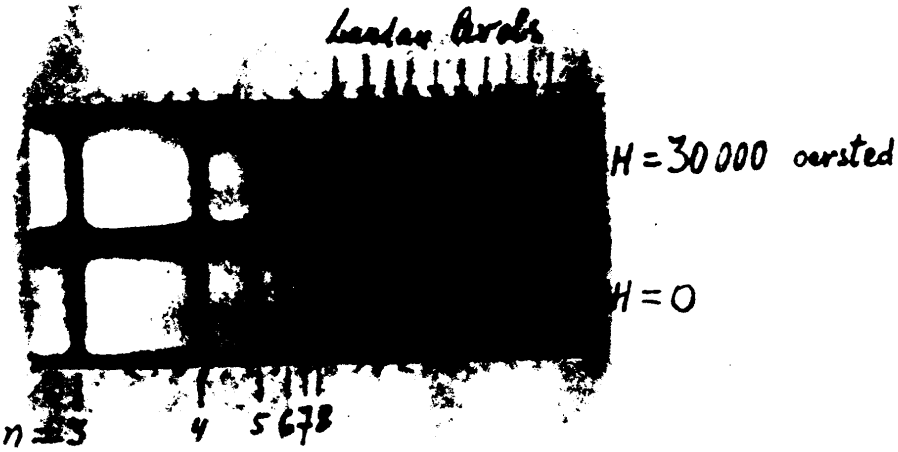

Fig 5

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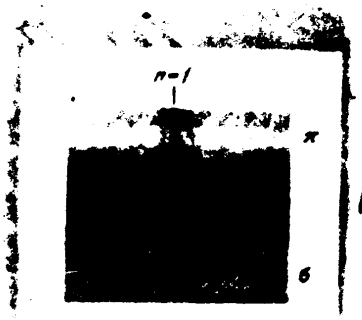

H = 32000 oersted

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Fig 6

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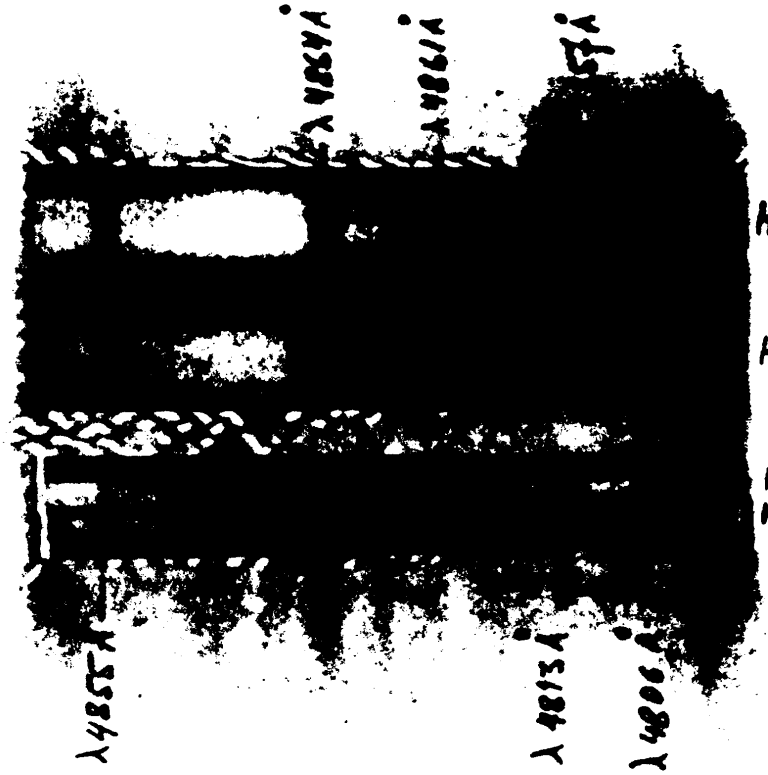

Fig. 7

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