INVERSE HYDROGENLIKE SERIES IN OPTICAL EXCITATION OF LIGHT CHARGED PARTICLES IN A BISMUTH IODIDE (BiI_3) CRYSTAL

E.F. Gross, V.I. Perel', and R.I. Shekhmamet'ev
A.F. Ioffe Physico-technical Institute, USSR Academy of Sciences; Leningrad State University
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In experimental investigations of the exciton states in a BiI_3 crystal, we have observed a hydrogenlike spectrum - a hydrogenlike series of resonance absorption and emission lines, converging not on the short-wave side of the spectrum, as usual, but on the long-wave side, something difficult to explain within the framework of the usual concepts. We describe here briefly this phenomenon and attempt to explain it as being due to excitation of light charged particles with negative effective masses by the light.

EXPERIMENTAL RESULTS

There are published data on the optical and photoelectric properties of bismuth iodide at temperatures above that of liquid helium [1 - 8].

We have previously investigated the spectra at T = 77°K, using single crystals and films of bismuth iodide [3 - 5].

The present experiments were made predominantly at liquid-helium temperature (4.2°K) and in part at higher temperatures up to T = 77°K, with BiI_3 single crystals grown from the gas phase [3].

The investigations of the optical spectra were made with unpolarized light traveling along the optical C axis of the crystal.

The spectra were investigated with an ISP-51 prism spectrograph with a camera having F = 1300 mm and with a dispersion 20 Å/mm in the investigated (red) region of the spectrum, and with a DFS-13 diffraction spectrograph with dispersion 1.9 Å/mm. The light source used to obtain the absorption spectrum was an incandescent lamp; luminescence excitation and added illumination of the crystals was with light from a DRSh-250 mercury lamp and optical filters.

In the absorption spectrum of single-crystal BiI_3 at T = 4.2°K we observed a group of five absorption lines[1]) lying in the long-wave side of the fundamental absorption edge, in the red part of the spectrum (see Figs. 1 and 2); this group vanished completely at T = 77°K (in liquid nitrogen). Following the line with the longest wavelength is a section of weak continuous absorption. An estimate of the absorption line widths gives on the average a value of approximately 10 cm^{-1} (for the first lines of the groups).

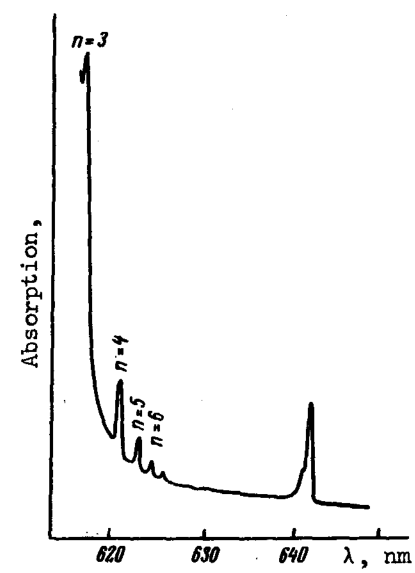

Fig. 1. Microphotogram of the absorption spectrum of single-crystal BiI_3 at T = 4.2°K. Dispersion 20 Å/mm.

[1])Other absorption lines, which are not discussed here, have also been observed in the spectrum.

Investigations of the influence of increasing the temperature and additional illumination of the crystal with radiation from the mercury lamp has revealed uniform shift of all the lines of the group towards the short-wave side of the spectrum[2] and a regular broadening, weakening, and gradual vanishing of the individual lines (starting with the "tail") of the group as a result of heating. This shows that the lines of the group are arranged in the spectrum not in a random fashion, but belong to a single system and are united by a single production mechanism. This group forms a series of lines that converge not in the short-wave side of the spectrum, as usual, but in the long-wave side. The frequencies ν_n of these lines obey the inverse serial dependence of the hydrogenlike atom:

$$\nu_n = \nu_\infty + \frac{R_1}{n^2} = 15978 + \frac{1995}{n^2}\ (\mathrm{cm}^{-1}), \qquad (1)$$

where n = 3, 4, 5, 6, 7, ...

As seen from the table, actually the frequencies of the lines experimentally measured by us agree well, within the limits of errors, with the values calculated from formula (1). In the luminescence spectrum of BiI_3 single crystals at T = 4.2°K we observed narrow emission lines[3], which resonantly coincide with the absorption lines of the inverse series (see the table).

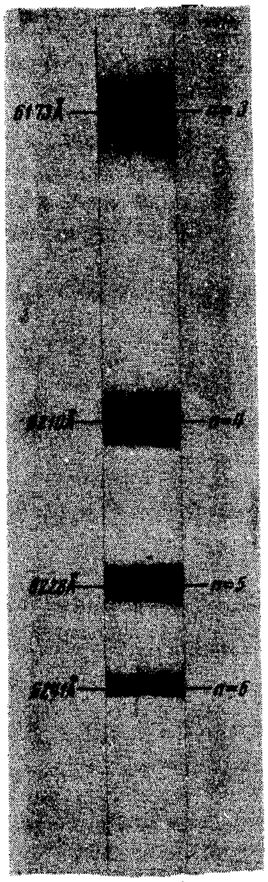

Fig. 2. Spectrogram of inverse series of absorption in a BiI_3 crystal at T = 4.2°K, obtained with a diffraction spectrograph having a dispersion 1.9 Å/mm.

The value of the Rydberg constant R_1 = 1995 cm^{-1} in formula (1) makes it possible to calculate the reduced effective mass of the system causing the occurrence of the series. Calculations give a value μ = 0.6 m for the reduced mass. This shows that light particles with masses close to the masses of the free electrons take part in the formation of the series.

DISCUSSION OF RESULTS

It is difficult to interpret the inverse sequence of the lines in the observed series.

In principle, such a sequence can be connected with the energy spectrum of two particles with like charges, having a negative reduced effective mass.

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[2]The boundary of the fundamental absorption is shifted in this case in an opposite direction, towards the long-wave side.

[3]The luminescence spectrum of BiI_3 crystals at T = 4.2°K, in which more than 30 narrow lines and bands were observed, will be given in a separate communication.

Positions of lines of the inverse series in the absorption and emission spectra of single-crystal BiI_3 at T = 4.2°K

Quantum numbers	Experiment			Calculations	
	Emission	Absorption			
	Wavelength	Wavelength	Frequency	Wave-length	Frequency
n	λ'_n, Å	λ_n, Å	ν_n, cm^{-1}	λ'_n, Å	ν_n, cm^{-1}
1	–	1)	–	5564	17973
2	–	1)	–	6069	16476
3	6174	6173 2)	16200	6173	16200
4	6211	6210 2)	16103	6210	16103
5	6229	6228	16056	6228	16057
6	6242	6241	16023	6237	16033
7	–	6246	16010	6243	16019
.	–	–	–	–	–
.	–	–	–	–	–
.	–	–	–	–	–
∞	–	6265	15961	6258	15978

1) The lines of the series with n = 1 and n = 2 were not observed because of the large absorption coefficient and the large thickness of the crystals.

2) The experimental values of the frequencies ν_3 and ν_4 were used to calculate the constants of the serial formula (1).

In fact, a system with a Hamiltonian

$$H = \epsilon(p) + \frac{e^2}{r},$$

where p is the quasimomentum, $\epsilon(p)$ the energy in the band, has a hydrogenlike spectrum with inverted arrangement of the levels, if $\epsilon(p) = E_0 - (p^2/2\mu)$, where μ is the reduced mass.

Such a system is quite unusual. Its discrete spectrum lies above the continuous spectrum, and the radius of the state is the smaller, the higher the energy. The system can consist of two electrons (it can then move, like a quasiparticle, through the crystal and it can be called a bielectron), or of an electron and a negatively charged center. At the present time there are no experimental grounds for assuming that a free bielectron appears in the optical spectrum.

The appearance of an inverse hydrogenlike series in the absorption spectrum can be due, for example, to the transition of an electron

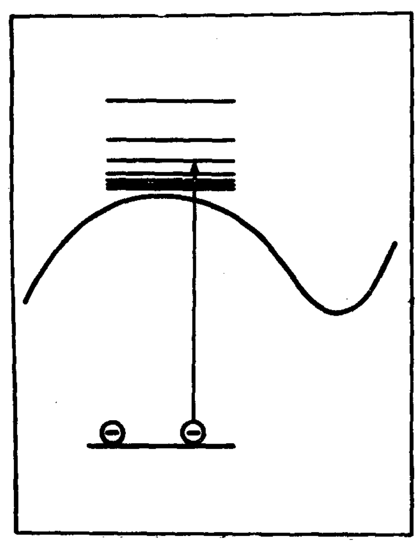

Fig. 3. Possible scheme that leads to the appearance of an inverse hydrogenlike series in the absorption spectrum.

from a doubly-negatively charged impurity center to discrete levels of state with negative mass in the field of the remaining singly-charged center (Fig. 3).

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