

Stark structure in the lines of the inverse hydrogen-like series in the spectrum of BiI₃ crystals

R. I. Shekhmamet'ev

Scientific-Research Institute of Physics, A. A. Zhdanov Leningrad State University

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A Stark structure has been discovered in the lines of the inverse hydrogen-like series in the absorption spectrum of BiI₃ at $T = 1.6$ K. This structure results from optical transitions to bielectron energy levels split by the crystal field. The anisotropy parameters A and the reduced masses μ_{\perp} and μ_{\parallel} are determined.

The inverse hydrogen-like series in the absorption spectra of semiconductors is characterized by a system with a negative reduced mass: a bielectron or bihole.^{1,2} Such systems may also include local centers which are sources of electrons (or holes) upon the formation of a bielectron (or bihole).^{1,3} In this case, the intensities of the lines of the inverse hydrogen-like series also depend on the concentration of centers.⁴

In an isotropic medium, the hydrogen-like energy levels of a bielectron (or bihole),

$$E_n = E_0 + G/n^2 ; \quad n = 1, 2, 3, \dots \quad (1)$$

($G = \mu'_0 e^4 / 2\hbar^2 \epsilon^2$ is the Rydberg constant of the system, μ'_0 is the reduced mass, and ϵ is the dielectric constant), have a degeneracy on the order of n^2 . In an anisotropic crystal the energy spectrum of a bielectron (or bihole) becomes more complex because the degeneracy with respect to l and m is lifted (l and m are respectively the orbital and magnetic quantum numbers).

The uniaxial BiI₃ crystal is an extremely low-symmetry crystal (space group C_{3i}^2), so that the energy levels are split by the internal crystal field. Optical transitions to these energy levels can lead to a complex pattern in the spectrum of the inverse

hydrogen-like series. According to the theoretical calculations of Ref. 5, however, allowed optical transitions to energy levels with $l > 0$ have probabilities significantly lower than those for transitions to S levels ($l = 0$). Accordingly, no Stark structure has previously been observed in the inverse hydrogen-like series in the spectra of BiI_3 . (The doublet structure in the principal lines of the inverse hydrogen-like series, with $n = 3 - 6$, has a different origin.⁶)

For a study of these possible optical transitions we synthesize BiI_3 crystals with a concentration of local centers substantially higher than in the samples which had been studied previously. We measured the spectra at temperatures of 1.6 and 4 K, using an instrument with a dispersion of 0.18 nm/mm. We used photographic recording of the spectra.

As the concentration of centers in the crystal is increased, a structure consisting of faint and narrow absorption lines "flares up" in the optical spectra of BiI_3 near principal lines of the inverse hydrogen-like series (Fig. 1). In general, this structure arises in a sequential fashion: first for the state with the principal quantum number $n = 6$ and then for states with $n = 5, 4$, and 3. The appearance of the structure and the intensification of the principal lines are accompanied by a simultaneous increase in the intensity in the narrow absorption band at 1.9808 eV, whose spectral position corresponds to the limit calculated from (1) for the inverse hydrogen-like series.¹⁾

The lines of this structure are grouped around the principal (intense) lines of the inverse hydrogen-like structure. The series consists of a system of Stark multiplets. A multiplet (a Stark multiplet) is constructed in the following way: There is an intense S line at the center (corresponding to an allowed band-band transition), and there are satellites (E_n^k) on each side of this principal line (E_n). These satellites are manifesta-

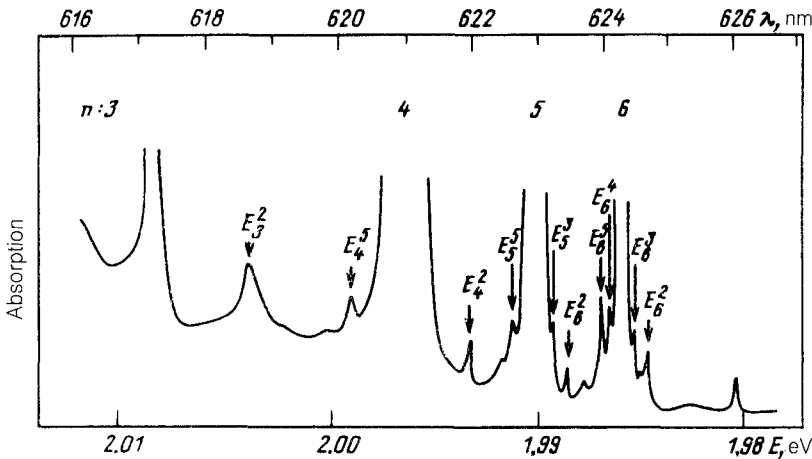


FIG. 1. Stark structure of lines of the inverse hydrogen-like series in the absorption spectrum of BiI_3 crystals at a temperature of 1.6 K. (Microdensitometer trace.) Here E_n^k are satellites of a multiplet, where n is the principal quantum number, and k is an arbitrary index.

TABLE I. Energies (in electron volts) of the principal lines E_n and satellites E_n^k of the Stark structure of the inverse hydrogen-like series in the absorption spectra of BiI_3 crystals at $T = 1.6$ K.

Quantum number	E_n	E_n^2	E_n^3	E_n^4	E_n^5
3	2.0084	2.0037	2.0060	2.0103	1)
4	1.9964	1.99352	1.99511	1.99792	1.99898
5	1.9900	1.98891	1.98968	1.99086	1.99163
6	1.9862	1.98503	1.98569	1.98694	1.98741

¹⁾The calculated position of the line with $E_3^5 = 2.0126$ eV falls in a region of strong absorption.

tions of states with higher values of the orbital quantum number ($P_0, P_{\pm 1}, D_{\pm 1}, D_{\pm 2}, |n \pm 0\rangle$, etc).¹⁾

The magnitude of the multiplet splitting, $\Delta E_n^k = |E_n - E_n^k|$, depends on the principal quantum number n —decreasing with increasing n . Measuring the positions of the lines in the BiI_3 spectrum at a temperature of 1.6 K, we found that the magnitudes of the multiplet Stark splitting of states with principal quantum numbers $n = 3, 4$, and 5 are greater than the splitting of the states with $n = 6$, by factors of about 4, 2.25, and 1.44, respectively (Table I). These results indicate a good adherence to the theoretical relation

$$\Delta E_n^k / \Delta E_{(n+1)}^k = (n+1)^2 / n^2, \quad (2)$$

which relates the n -dependent magnitudes of the multiplet splitting of the energy levels of the hydrogen-like system in an anisotropic uniaxial crystal.^{7,8}

In a uniaxial crystal, the positions of the Stark energy levels of a hydrogen-like system (e.g., a Wannier exciton) can be described in first-order perturbation theory⁸ with the help of an anisotropy parameter $A = \epsilon_{\perp} \mu_{\perp} / \epsilon_{\parallel} \mu_{\parallel}$ by formulas of the type

$$E_1^{n|l|m|} = E_0^{n00} [K_{l|m|} f^{l|m|}(A) - 1], \quad (3)$$

where $\mu_{\parallel}, \mu_{\perp}$ and $\epsilon_{\parallel}, \epsilon_{\perp}$ are the values of the reduced masses and dielectric constants along the optic axis of the crystal and perpendicular to it; E_0^{n00} is the energy of the unperturbed level with principal quantum number n ; $f^{l|m|}(A)$ is a function which depends on the anisotropy parameter A and the quantum numbers l and m ; and $K_{l|m|}$ is a numerical factor.

Analysis of the formulas from Ref. 8 shows that the l and m splitting of the energy levels of a bielectron is basically the same as the splitting of the energy levels of an exciton in an anisotropic crystal. We can thus determine the parameter A by using (3) and taking account of the direction in which the series converges.

This tentative interpretation of the lines in the structure of the inverse hydrogen-

like series leads to estimates of A between 2.0 and 2.6 and allows us to calculate the reduced masses μ_{\perp} and μ_{\parallel} from the relation in Ref. 7:

$$1/\mu_0 = 2/3\mu_{\perp} + \epsilon_{\perp}/3\mu_{\parallel}\epsilon_{\parallel}. \quad (4)$$

For the case with¹ $A = 2.6$ and $\mu'_0 = 0.6 m_0$ we find the values $\mu'_1 = 0.91 m_0$ and $\mu'_{\parallel} = 0.42 m_0$. (In determining the parameter A , we used the constant $G = 0.3306$ eV found from the experimental position of the principal absorption lines with $n = 5$ and $n = 6$ in the inverse hydrogen-like series and the values of the dielectric constants $\epsilon_{\perp} = 6.15$ and $\epsilon_{\parallel} = 5.19$ from Ref. 9.)

It also follows from the theory of Ref. 8 that at $A > 1$ the binding energy calculated from (3) must be smaller than that found in the isotropic case. A shift of this sort of the lines of the inverse hydrogen-like series with respect to the positions calculated from (1) is indeed observed¹ in the spectra of BiI_3 . We conclude by noting that some of the lines have also been observed previously in the spectra of BiI_3 crystals (e.g., the line with $\lambda = 618.8$ nm or the Q line), but the nature of these lines has remained unclear. These lines now fit in a natural way into the Stark structure of lines of the inverse hydrogen-like series.

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¹Analogous phenomena have been observed in the spectra of resonant luminescence.

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