Inverse hydrogen-like series in the optical spectra of ZnP_2 crystals

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A series of eight absorption lines observed near the fundamental absorption edge of the monoclinic ZnP_2 crystal converges on the long-wave side. This series can be described by the formula for a hydrogen-like formation with a negative reduced mass. The results are interpreted with reference to a model of a bielectron–impurity complex.

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In a 1971 study[1] of the optical spectra of BiI_3 crystals near the fundamental absorption edge, Gross *et al.* found a hydrogenlike series of four resonant absorption and emission lines which converged on the long-wave side, rather than on the customary short-wave side. In an effort to explain this very unusual result, Gross *et al.*[1] suggested that the inverse hydrogenlike series reflects the energy spectrum of two charged particles of like charge which have a negative reduced effective mass. The possible existence of such a system had been discussed earlier by Rashba and

Edel'shtein[2] in connection with an analysis of magneto-Coulomb levels near saddle points.

In several subsequent papers,[3] the experimental results of Ref. 1 were interpreted on the basis of a model of a bielectron (or bihole) bound state of two electrons (or two holes) from different conduction bands (or valence bands). Later papers,[4,5] however, questioned whether the lines observed in BiI_3 were of a common nature. Furthermore, BiI_3 has been the only crystal for which the question of an inverse hydrogen like series has arisen at all.

In this letter we are reporting the first study of an inverse hydrogenlike series in monoclinic ZnP_2 crystals (black modification, C_{2h}^5 symmetry), which are quite different from BiI_3 in both chemical composition and structure. The ZnP_2 crystals which we studied, grown from the gas phase, exhibited an *n*-type conductivity with a carrier concentration of 10^{14}-10^{16} cm^{-3}. Spectra were measured at temperatures of 2 and 77 K with an apparatus using a DFS-24 spectrometer with a slit having a spectral width of 0.2 Å.

Figure 1 shows the transmission spectra of the monoclinic ZnP_2 crystal (the polarization is $\mathbf{E}\perp C_2$; the light propagation direction is $\mathbf{K}\perp C_2$) at 2 K (curves a and a′) and 77 K (curve b). We see that there are groups of lines having a similar structure. The most intense and the shortest-wave lines of these groups, the "head" lines (marked by the vertical arrows at the bottom of Fig. 1), form a series which converges on the long-wave side. As the temperature is raised from 2 to 77 K, the number of lines in the groups falls off substantially. All the head lines undergo a parallel long-wave shift of about 4 meV, as do the exciton reflection lines in the spectral region $\lambda < 8000$ Å (Refs. 6 and 7). The positions of the head lines can be described well by

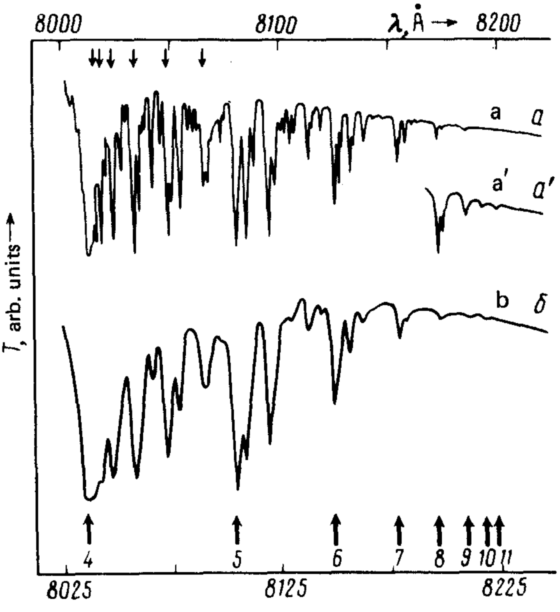

FIG. 1. Transmission spectra of the monoclinic ZnP_2 crystal on the longwave side of the fundamental absorption edge in the polarization $\mathbf{E}\perp C_2$. a,a′–$T = 2$ K (the upper λ scale); b–77 K (the lower λ scale). a,b–Crystal thickness $d = 0.9$ mm; a′–$d = 0.9$ mm.

the formula of the inverse hydrogenlike series, $\mathcal{E} = \mathcal{E}_g^{(ee)} + G^{(ee)}/n^2$, if the lines are numbered $n = 4$ (for the shortest-wave line) to $n = 11$ (for the longest-wave line). At $T = 2$ K we then find $\mathcal{E}_g^{(ee)} = 1.504$ eV and $G^{(ee)} = 0.733$ eV.

With regard to the positions of the constituent lines, we note that in the short-wave groups we can distinguish series of lines which converge on the short-wave side. This tendency is particularly clear at $T = 77$ K in the $n = 4$ group (the corresponding lines are marked by the vertical arrows at the top of Fig. 1). As the temperature is lowered to 2 K, additional lines appear, but the most intense of these lines are those which were observed at 77 K. Analysis of the spectral positions of the constituent lines with the help of the formula for the (forward) hydrogenlike series, $\mathcal{E} = \mathcal{E}_g^{(n)} - G^{(n)}/K^2$, indicates a significant deviation from a hydrogenlike behavior if we choose as $\mathcal{E}_g^{(n)}$ the spectral position of the head line n.

The existence of a clearly defined inverse hydrogenlike series suggests that the spectrum is formed by a mechanism of the bielectron type. Such a mechanism is consistent with the n-type conductivity of these samples. In this case the band scheme of the ZnP_2 crystal, which determines the optical properties of this crystal near the fundamental absorption edge,[6] can be described (Fig. 2) as consisting of two conduction bands, C_1 and C_2, with one or two nearby valence bands V. If a bound state of electrons from C_1 and C_2 is to form, the corresponding effective masses must satisfy the inequalities $m_1 > |m_2|$ and $m_2 < 0$.

Using the measured values of $G^{(ee)}$, and adopting a static dielectric constant of 10, we can estimate the reduced bielectron mass to be $\mu_{ee} \approx 5.4 m_0$, where m_0 is the mass of the free electron, and we can estimate the first Bohr radius of the bielectron to be $a_{ee}^{(1)} \approx 1$ Å. The radius of the observed $n = 4$ state is then $a_{ee}^{(4)} \approx 16$ Å; i.e., the most intense observable bielectron states should have relatively small radii.

As it enters the field of a positively charged center (an ionized donor, for example), the bielectron behaves at a large distance as if it were a point charge $-2e$ with an effective translational mass $M_{ee} = m_1 - |m_2| > 0$. The result is the formation of an ordinary hydrogenlike system with an attractive potential. If $\mu_{ee} \gg M_{ee}$, the bielectron should retain its individual properties to a large extent, and this is what we see

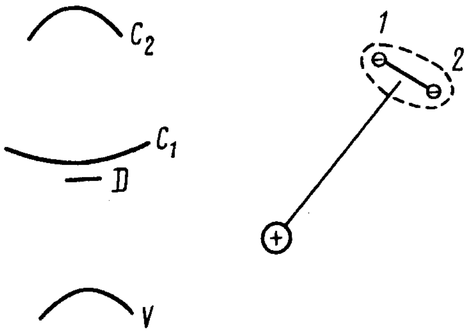

FIG. 2. A band scheme for the monoclinic ZnP_2^2 crystal which permits the formation of a bielectron–impurity complex, shown at the right. C_1, C_2 –Conduction bands; V–valence band; D–energy level of the neutral donor.

in the inverse hydrogenlike series. On the other hand, because of the interaction of the bielectron as a unit with the positively charged center there may be forward hydrogenlike series, which should lie on the long-wave side of each bielectron (head) absorption line.

A more careful analysis of the many-body interaction in a bielectron-impurity complex of this type should result in deviations from a hydrogenlike behavior, and we are apparently seeing such deviations in the positions of the constituent lines. As the temperature is lowered, it may be possible to see some subtler spectral details, caused (for example) by a lifting of the orbital degeneracy of this bielectron-impurity complex.

The conditions for the optical excitation of this complex are determined by the initial state of the system. Such a state may be formed, for example, by a complex D^- consisting of a C_1 electron bound to a neutral donor D whose level is below band C_1 (Fig. 2). In this case the value of $\mathscr{E}_g^{(ee)}$ found from the formula for the inverse hydrogenlike series should exceed the energy gap between the extrema of the C_1 and C_2 bands by an amount equal to the dissociation energy of the D^- complex.

At this point, unfortunately, we do not have reliable data on the band structure of monoclinic ZnP_2 crystals, and in fact we have extremely little experimental information of any sort. Consequently, our suggestions regarding the nature of the long wave absorption spectra of these crystals require a more detailed experimental study.

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