Inverse hydrogen-like spectrum of ZnP_2 in a magnetic field

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Optical transitions associated with the excitation of singlet (S) and triplet (T) bielectron states of monoclinic ZnP_2 crystals have been identified. The spectroscopic g-factors of the splitting have been found: $g_S = 0$ and $g_T = 4$.

The inverse hydrogen-like series of states observed in the optical spectra[1] of monoclinic ZnP_2 crystals is interpreted on the basis of the concept of a bielectron[2]: a two-electron complex with a negative reduced mass. The model of a bielectron-impurity complex, i.e., a bielectron bound to a positively charged center, was first proposed by Sel'kin *et al.*[1] to explain the complex structure of the inverse hydrogen-like spectrum in ZnP_2. According to this model, an optical transition involving the absorption of a photon occurs from the ground state of a shallow center with two band electrons of the lowest conduction band into a state of a bielectron-impurity complex, in which one of the electrons belongs to the upper conduction band with a negative effective mass.

If the distance from the core of the center to the bielectron is substantially greater than the size of the bielectron, we can expect to find in the optical spectrum, along with intense (head) lines of the inverse hydrogen-like series, evidence of additional satellite lines which converge in the short-wave direction and which lie on the long-wave side of each head line.[1,3,4]

Figure 1a shows a typical transmission spectrum of a monoclinic ZnP_2 crystal ($T = 2$ K) in light of polarization $\mathbf{E} \perp \mathbf{b}$ ($\mathbf{b}$ is the twofold monoclinic axis) which is propagating along the direction $\mathbf{K} \perp \mathbf{b}$. The number $n = 4, \ldots, 10$ specifies the head line in the formula for the inverse hydrogen-like series.[1] The satellite lines $a, b, c, \ldots$, which converge in the short-wave direction, can be seen most clearly in the $n = 4$ fragment.

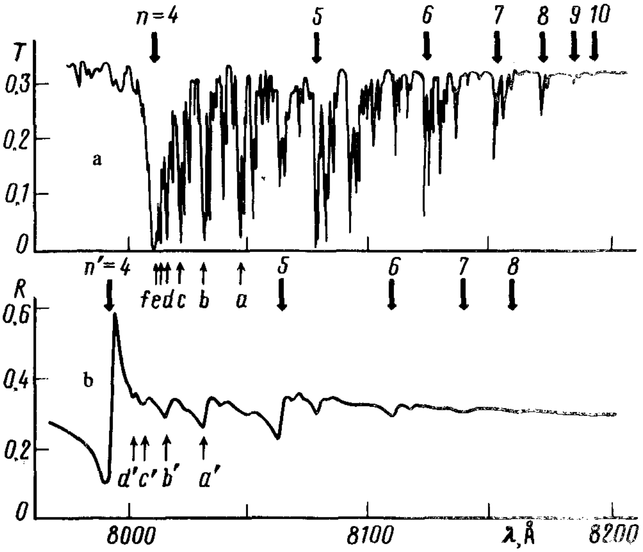

FIG. 1. Transmission (a) and reflection (b) spectra of a monoclinic ZnP_2 crystal 0.2 mm thick, recorded at $T = 2$ K in an arrangement with (a) $\mathbf{K}\perp\mathbf{b}$, $\mathbf{E}\perp\mathbf{b}$ and (b) $\mathbf{E}\|\mathbf{b}$, where **b** is the twofold crystallographic axis.

It is not possible to measure the transmission spectrum in the polarization $\mathbf{E}\|\mathbf{b}$ because of the strong optical absorption. In the $\mathbf{E}\|\mathbf{b}$ reflection spectrum (Fig. 1b) we see a clearly defined structure, in which we can also identify the head lines of the inverse hydrogen-like series with $n' = 4, \ldots, 8$, along with the adjacent satellite lines (in the $n' = 4$ fragment, the lines a', b', ...).

It can be concluded from these results that in these ZnP_2 crystals the optical transitions to the n' states ($\mathbf{E}\|\mathbf{b}$) are dipole-active, while those to the n states ($\mathbf{E}\perp\mathbf{b}$) are dipole-forbidden. According to our model of a bielectron-impurity complex,[1] the forbidden optical transition $\mathbf{E}\perp\mathbf{b}$ involves a flipping of the electron spin, while the allowed transition $\mathbf{E}\|\mathbf{b}$ occurs without a change in the spin state of the system. If the ground state of the center is a singlet state, the excited state (a bielectron state) is a singlet of polarization $\mathbf{E}\|\mathbf{b}$ and a triplet in the polarization $\mathbf{E}\perp\mathbf{b}$.

The lines n' in the polarization $\mathbf{E}\|\mathbf{b}$ are shifted in the short-wave direction from the corresponding lines n in the polarization $\mathbf{E}\perp\mathbf{b}$. The magnitude of this shift decreases as we go to longer-wave fragments. A similar behavior is seen in the $\mathbf{E}\perp\mathbf{b}$ and $\mathbf{E}\|\mathbf{b}$ luminescence spectra, which we are not reproducing here.

The apparent reason for the observed shift between the n' and n lines is an exchange singlet-triplet splitting, to which there are contributions from both the short-range component of the exchange interaction and its long-range component (this component, which is due to the dipole nature of the transition for $\mathbf{E}\|\mathbf{b}$, leads to longitudinal-transverse splitting effects). With increasing n, there is an increase in the radius of the Bohr orbit in the bielectron, and the exchange interaction becomes weaker as a result. This effect explains the decrease in the relative shift between the n' and n lines as we go to longer-wave fragments in the spectrum.

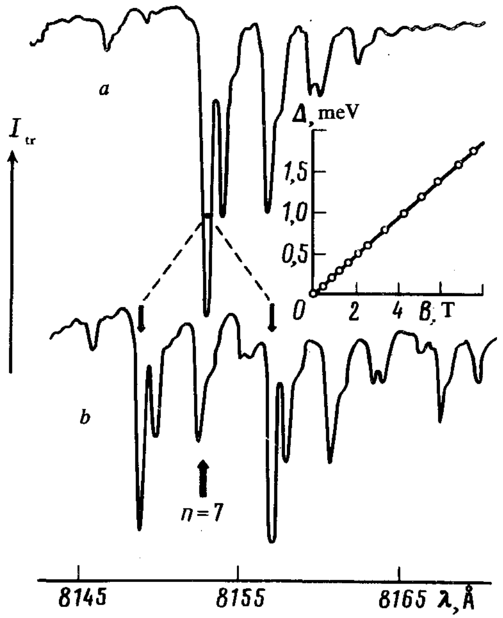

FIG. 2. Effect of an external magnetic field on the transmission spectrum of a ZnP_2 crystal in the region of the $n = 7$ fragment ($\mathbf{K}\perp\mathbf{b}$, $\mathbf{E}\perp\mathbf{b}$, $\mathbf{B}\parallel\mathbf{b}$). *a*—$\mathbf{B} = 0$ T; *b*—$\mathbf{B} = 6.72$ T. The inset shows the doublet splitting (Δ) of the $n = 7$ head line of the inverse hydrogen-like series versus the magnetic induction $\mathbf{B}$.

To test these suggestions regarding the nature of the observed spectra, we studied the effect of a magnetic field on the spectra in Fig. 1, at magnetic inductions $\mathbf{B}$ up to 7.6 T. With $\mathbf{B}\parallel\mathbf{b}$, in light of polarization $\mathbf{E}\perp\mathbf{b}$, we observe a doublet splitting of all the spectral lines, and this splitting is linear in the field; in the polarization $\mathbf{E}\parallel\mathbf{b}$, the spectrum exhibits no noticeable changes when an external magnetic field is applied. Figure 2 shows, for the particular case of the $n = 7$ fragment, how the magnetic field affects the transmission spectrum of the ZnP_2 crystal in light of polarization $\mathbf{E}\perp\mathbf{b}$.

Analysis of the transmission spectra shows that all the lines, including the satellite lines, are split by the magnetic field into doublets with the same g factor, 4. The inset in Fig. 2 shows the doublet splitting Δ of the $n = 7$ head line versus the magnetic induction $\mathbf{B}$. From this plot we find the value $g = 3.99 \mp 0.01$. Returning to the scheme under consideration here for the optical transition, and noting that we have $g = 0$ in the polarization $\mathbf{E}\parallel\mathbf{b}$, we conclude that the g factors of the electrons of the lower and upper conduction bands, which form the bielectron state, are identical, equal to 2.

The intensities of the split components of each line in the transmission spectrum are essentially identical (Fig. 2*b*). It follows that the initial state in the transition under consideration is a singlet state, while the excited state is a triplet state. Further evidence that the excited state is of a triplet nature in the case of the optical transition in the polarization $\mathbf{E}\perp\mathbf{b}$ comes from the relative intensities of lines in the luminescence spectrum: The shorter-wave emission line in a doublet split by a magnetic field is much less intense than the long-wave line.

In summary, our magneto-optical studies of the transmission, reflection, and luminescence spectra of ZnP_2 crystals confirm our model of the optical transition to a state of a bielectron-impurity complex, which generates the observed spectra. For the first time, we have reported here experimental data which indicate the existence of both singlet and triplet states of a bielectron. Further important information on the nature of the unusual spectra of these crystals may emerge from a systematic study of the actual centers which are responsible for the formation of the bielectron-impurity complexes.

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